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MODERN CHEMICAL PROCESSES

A Series of Articles Describing
Chemical Manufacturing Plants

*by the Editors of
Industrial and Engineering Chemistry
in conjunction with the technical staffs
of the cooperating organizations*

VOLUME V

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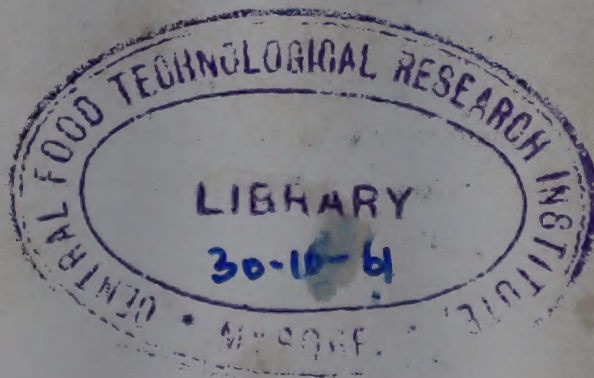
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Modern chemical...

FOREWORD

The appearance of this volume of "Modern Chemical Processes" means that a full decade has passed since the conception of the Staff-Industry Collaborative Report became a reality. The editors of *Industrial and Engineering Chemistry* are very proud of this series. Time has not dulled its impact or its interest. We receive frequent requests for reprints of Reports which were published in the very early stages of the series. This simply means that even years later much of the basic information reported is good and current. We intend to keep the series this way.

This volume is thinner than previous volumes. One of the reasons is that our high editorial standards have forced us to reject some articles when they were ready to go to the printer. Another reason is an improved approach. We have tried to streamline these articles, to present them in the most interesting way, and to keep in mind the busy reader. We have not sacrificed pertinent information, but we have removed unnecessary detail, and used graphical methods which would give the reader an almost automatic self-screening device.

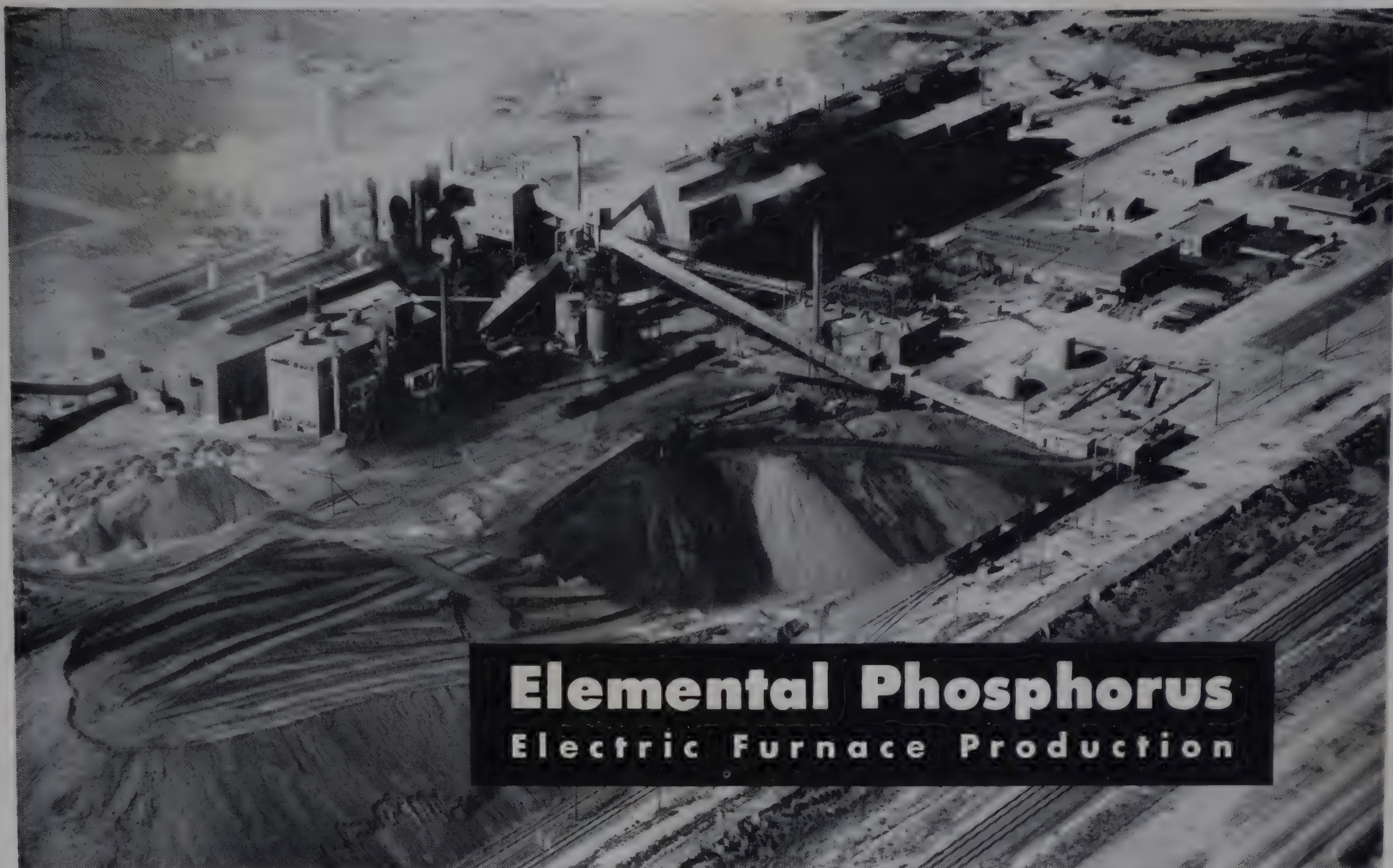
As the Staff-Industry Collaborative Report series enters its second decade, we expect, with an expanded staff, to continue to give I/EC's readers the very best in detailed descriptions of operating plants in the chemical process industries. We are indeed grateful to the companies whose vision enables them to release to us and the permanent literature information which is of great interest. We are grateful to their staff members who spend much time with our own editors in bringing these stories to completion. Collaboration is a word which still has unpleasant connotations. In this Report series we think the opposite extreme is reached.

WALTER J. MURPHY
Editorial Director

Washington, D. C.
May 20, 1958

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Elemental Phosphorus

Electric Furnace Production

GORDON H. BIXLER, Associate Editor

in collaboration with

JOSIAH WORK AND R. M. LATTIG

Westvaco Mineral Products Division, Food Machinery & Chemical Corp., Pocatello, Idaho

PICK any major industry today, and even many a minor one, and chances are one or more phosphate chemicals occupy an important position in it. From early use as a fertilizer, phosphorus is now a key element in water softeners and detergents, food chemicals, metal coating chemicals, metal alloying, insecticides, plasticizers, lubricants, fuel additives, fire retardants, pharmaceuticals, and pyrotechnics, to name only a few.

Until about two decades ago, the phosphate industry of the United States was practically synonymous with wet process acidulation. Elemental phosphorus has been produced by electric furnace continuously in the United States since 1897, but not until the 1930's did elemental phosphorus begin its burgeoning growth. The advent of cheap hydroelectric power, develop-

ment of improved electric techniques by Tennessee Valley Authority, and growing outlet for phosphates in detergents and water treatment combined to account for sharp increases in this 20-year period.

Today, elemental phosphorus production is approaching the 300,000-ton-per-year level, and seven companies now operate 27 electric furnaces having a design rating of close to 450,000 kv.-amp. One additional furnace is under construction. Of these producers, Westvaco Mineral Products Division, Food Machinery & Chemical Corp., has the largest installation in the West (at Pocatello, Idaho) and is the third largest producer in the country.

Elemental Phosphorus Production in United States^a

Year	Tons	Year	Tons
1939	43,000	1947	85,940
1940	48,500	1948	112,000
1941	56,135	1949	138,000
1942	71,612	1950	153,233
1943	79,262	1951	184,693
1944	85,679	1952	195,157
1945	80,000	1953	253,726
1946	83,500	1954	266,887

^a (1, 3, 4, 6, 8)

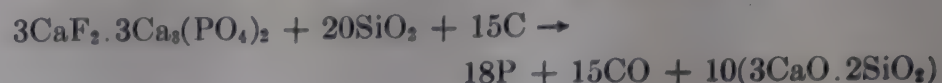
Phosphorus exists in nature only as phosphate because of its extreme reactivity with oxygen. As a solid, it may be in one of at least four allotropic forms—alpha and beta white, black, or red. White phosphorus, however, is the most common form and the one implied by the term “phosphorus.” It is a white-to-yellow solid melting at 44.1° C. and boiling at 280.5° C. Properties of phosphorus as well as some of its compounds have been compiled in convenient form by Tennessee Valley Authority (9), and the entire technology of the phosphorus and phosphates industry is the subject of an AMERICAN CHEMICAL SOCIETY monograph by Waggaman (11).

Phosphate ore is an apatite mineral of marine sedimentary origin. Because of variable composition, no definite chemical formula can be assigned to it, but it can be represented as $\text{Ca}_{10}(\text{PO}_4\text{CO}_3)_6(\text{F}, \text{Cl}, \text{OH})_2$. Fluorapatite, with a nominal composition of $\text{Ca}_5(\text{PO}_4)_3\text{F}$, is the most prevalent form.

Phosphorus production involves replacement of the phosphoric acid in phosphate-bearing materials by another acid, with simultaneous reduction of the liberated acid (as phosphorus pentoxide) at high temperature with coke or other form of carbon. Early technology called for treating bones with sulfuric acid, filtering the resultant gypsum and other insolubles from phosphoric acid, concentrating the acid by evaporation, and finally retorting the concentrated acid in presence of carbon to effect reduction to elemental phosphorus. This process has been entirely supplanted by electric smelting.

In electric furnace smelting, advantage is taken of silica's acting as a strong acid at high temperatures. At 1300° to 1500° C., silica liberates phosphorus pentoxide from phosphate rock, and the phosphorus pentoxide is then reduced by coke present in the furnace charge. The exact reaction mechanism is not fully understood, however. Because of the variable nature of phosphate

rock, a number of reactants are formed, especially different calcium silicates. The over-all simplified reaction is:



The same result can be achieved using incandescent coke instead of electricity as a heat source. However, few blast furnaces for elemental phosphorus production were ever built, and the last—operated by Victor Chemical Works primarily for acid production—ceased operation in 1940.

First electric furnace for elemental phosphorus production in the United States was constructed by Oldbury-Electro-Chemical Co. at Niagara Falls, N. Y., in 1897, and Oldbury remained the sole elemental phosphorus producer in the U. S. until the end of World War I. Oldbury now has three furnaces in operation at Niagara Falls.

Postwar entrants to the phosphorus industry were Theodore Swann's Federal Phosphorus Co. at Anniston, Ala., in 1919 and Victor Chemical Works in 1930 at Nashville, Tenn. Swann is among pioneers who developed the electric furnace for phosphate rock reduction, while Victor originally took the blast furnace route. Both these companies recovered phosphoric acid instead of taking the reaction through to elemental phosphorus (a small part of the phosphorus produced in the Victor furnace was condensed and removed from the system before the major part was burned to acid). They bear mentioning as important steps in elemental phosphorus development, however, for Monsanto Chemical Co. acquired the Swann company as its entree to the elemental phosphorus industry, while Victor ceased its blast furnace operation when it put its first electric furnace in operation at Mt. Pleasant, Tenn.

Tennessee Valley Authority has been intimately connected with development of elemental phosphorus production techniques since 1934 (10). TVA interest in elemental phosphorus develop-

Elemental Phosphorus Producers

Company	Location	First Operation	Rating, Kv.-Amp.	Type Furnace
Westvaco Mineral Products Division	Pocatello, Idaho	1949	18,000	TVA No. 6
		1950	20,000	TVA No. 6
		1951	25,500	TVA No. 6
		1952	36,000	Round
Monsanto Chemical Co.	Monsanto, Tenn.	1937	8,000	Round
		1937	8,000	Round
		1937	8,000	Round
		1941	20,000	Round
		1948	25,000	Round
		1950	25,000	Round
	Monsanto, Idaho	1952	30,000	Round
		1954	30,000	Round
Victor Chemical Works	Mt. Pleasant, Tenn.	1938	12,000 ^a	
		1940	12,000 ^a	
		1940	12,000 ^a	
		1941	12,000 ^a	
	Tarpon Springs, Fla. ^b	1947		
		1951	25,000	
	Silver Bow, Mont.	1952	25,000	
		1953	32,000	TVA No. 6
Shea Chemical Corp. ^c	Columbia, Tenn.			Round
Oldbury Electro-Chemical Co.	Niagara Falls, N. Y.	^d	16,000	Round
Virginia-Carolina Chemical Corp.	Nichols, Fla.	1937	12,000 ^e	Round
American Agricultural Chemical Co.	Charleston, S. C.	1950		TVA No. 6
	Pierce, Fla.	1952	7,500	TVA No. 6
		1955	12,000	TVA No. 6

^a Design rating of these furnaces was 7600 kv.-amp. when installed. Each was boosted to 12,000 kv.-amp. in 1947.

^b Design rating of this furnace has not been revealed, except that it is larger than the Mt. Pleasant furnaces.

^c Second furnace, of 42,000 kv.-amp., is scheduled for completion in July 1956.

^d Oldbury's first furnace began operating in 1897. A number of others built since then have been superseded by the three presently operating.

^e Estimated rating, based on estimated annual production of 14,000 tons, a power factor of 90%, and 5.9 kw. per pound of phosphorus produced.

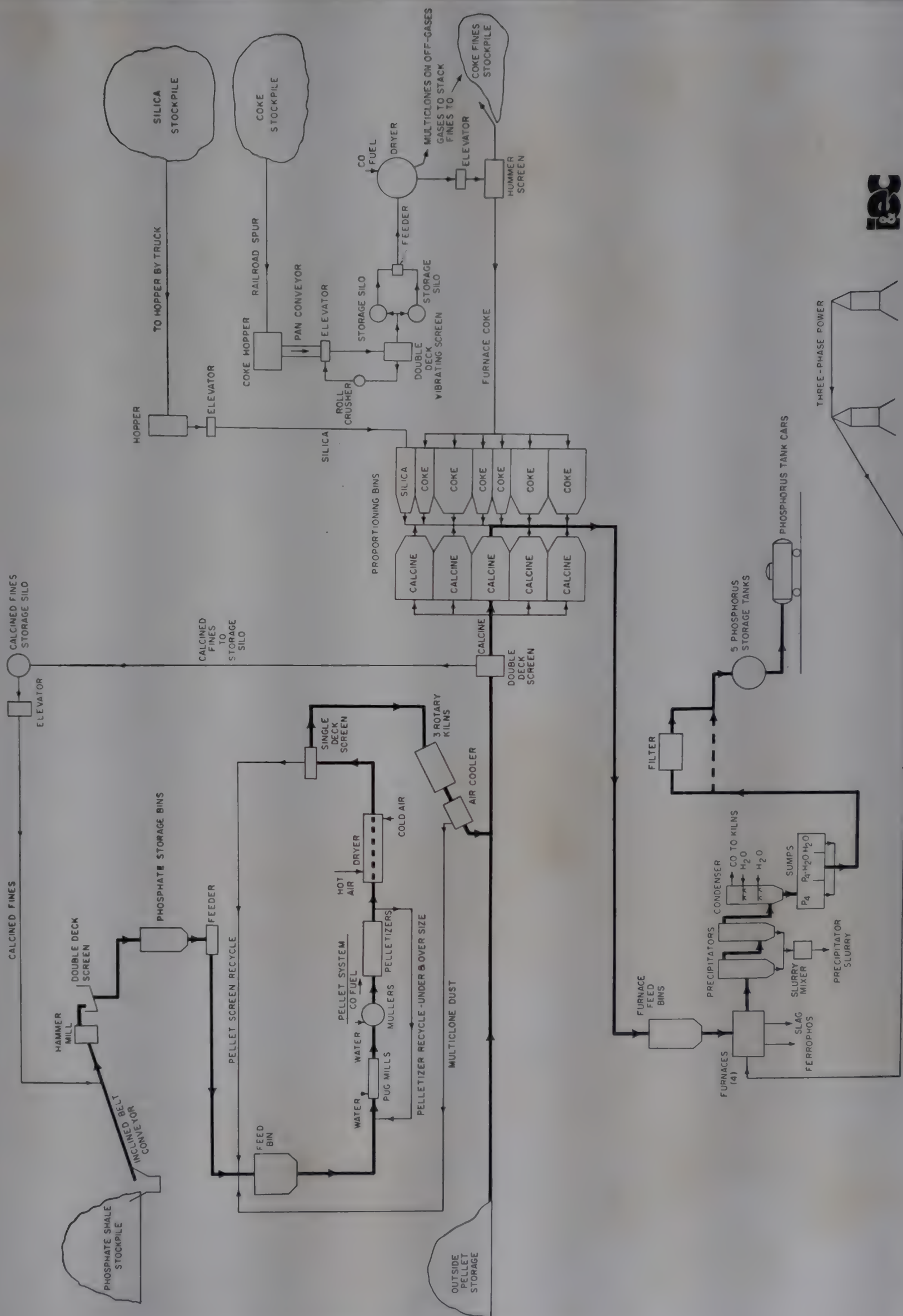


Figure 1. Flow sheet for production of elemental phosphorus by electric furnace by Westvaco Mineral Product Division, Food Machinery & Chemical Corp, Pocatello, Idaho

ment stemmed primarily from a desire to produce phosphate fertilizers of higher concentration at less expense. During its development program, TVA built and operated nine furnaces. Of the 27 furnaces now operated by industry, seven are based essentially on what is known in the industry as "TVA Furnace No. 6," as is the furnace now being built by Shea Chemical.

While the TVA contribution to elemental phosphorus production has been extensive, only during the past three years has elemental phosphorus become of commercial importance in fertilizer manufacture. In 1952, Agriform Co. introduced neutral fertilizer solutions in California. These were made by reacting ammonia with phosphoric acid produced by Westvaco from elemental phosphorus. This development awaited availability of white acid, since green acid from wet process acidulation results in formation of flocculent, ammonia-complex precipitates. Elemental phosphorus did not achieve prominence earlier in fertilizer manufacture because it was not sufficiently available for such use.

Among elemental phosphorus producers, Monsanto is the largest. Starting with three furnaces at Monsanto, Tenn., it now has six, plus two additional furnaces at Monsanto, Idaho. Victor Chemical Works is second largest, with four furnaces at Mt. Pleasant, Tenn., one at Tarpon Springs, Fla., and two at Silver Bow, Mont.

Virginia-Carolina Chemical Corp. has two furnaces, one at Charleston, S. C., and one at Nichols, Fla. The latter is an old one dating from 1937, purchased by V-C along with certain phosphate properties when it acquired Phosphate Mining Co. in 1946. The Charleston furnace was constructed by V-C in 1950.

American Agricultural Chemical Co. started producing phosphorus at South Amboy, N. J., in 1935 and supplemented its production with a new furnace at Pierce, Fla., in 1952. Since then the South Amboy operation has been discontinued, and AAC put its second furnace on the line at Pierce last month.

Newest major producer is Shea Chemical Corp. Its first furnace began operation at Columbia, Tenn., in 1953, and a second will go on the line there in July this year.

Interest of Westvaco in phosphate chemicals dates from 1887 when a predecessor company was formed to manufacture mono-, di-, and trisodium phosphate for use in water softeners, products which remained the company's principal ones up to the early 1930's.

In 1948, Westvaco began an across-the-board expansion in phosphate chemicals, key unit of which was a new elemental phosphorus plant at Pocatello, Idaho. Construction began in July 1948, and the first furnace came on the line 13 months later. (In the interim, Westvaco merged with Food Machinery.) Additional furnaces were brought into production in February 1950, May 1951, and November 1952. Two new plants for manufacture of phosphoric acid and molecularly dehydrated phosphates were put into operation at Newark, Calif., in 1948 and at Lawrence, Kan., in 1949. Westvaco's elemental phosphorus production exceeded the 100,000,000-pound level last year.

Phosphate rock occurs in many countries of the world, with French Morocco, United States, USSR, Tunisia, and Algeria each

Five major processing steps:

Mining and stockpiling

Sizing and agglomerating furnace feed

Proportioning shale, coke, and silica feed material

Smelting

Recovery

having reserves estimated at more than 1,000,000,000 metric tons. Of these, the U. S. is second (to French Morocco) with reserves of 13,526,000,000 metric tons (8).

Phosphate mining of commercial importance has occurred in 16 states. At the present time, however, only deposits of Florida, Tennessee, and the four-state area of Montana, Idaho, Utah, and Wyoming are commercially important. Need for cheap hydroelectric power and cheap phosphate rock has caused the center of gravity of the phosphorus industry gradually to shift westward. Up to the early post World War II years, Tennessee enjoyed triple advantages of low cost power, readily available ores, and nearby markets. While Tennessee operations are by no means being abandoned, greatest activity in bringing in new phosphorus facilities centers in the western fields.

Western phosphate deposits cover the four states in a roughly north-south area about 200 miles wide and 400 miles long. In contrast to phosphate shales elsewhere in the U. S., western shales contain a significant amount of vanadium, and it is believed organisms which formed the western deposits had vanadium in their blood instead of iron. Western shales also have a higher content of organics than do other U. S. shales.

Prior to Westvaco's production of elemental phosphorus at Pocatello, all phosphate activity in western fields was devoted to reclaiming high grade rock suitable for wet process acidulation and for production of vanadium oxide. Where low grade shales were stripped from high grade rock layers, they were either stockpiled or used as back-fill. Westvaco is the only company today using low grade shales as such. Both Victor at its underground mine at Melrose, Mont., and Monsanto in its open pit mine at Soda Springs, Idaho, recover both high grade phosphate rock and low grade shales and use the combined materials as furnace feed.

At the Westvaco plant, shale and coke are received by rail and silica by truck and stockpiled. Shale is reclaimed from the stockpile and crushed. Material of a size suitable for feeding directly to the furnaces (phosphate lump) goes to kilns for calcining. Undersize (phosphate fines) is mixed with water, pelletized in rotating drums, and calcined. Calcined pellets and lump, known collectively as nodules, go to the proportioning building. Meanwhile, coke is sized and dried, silica is sized, and both also

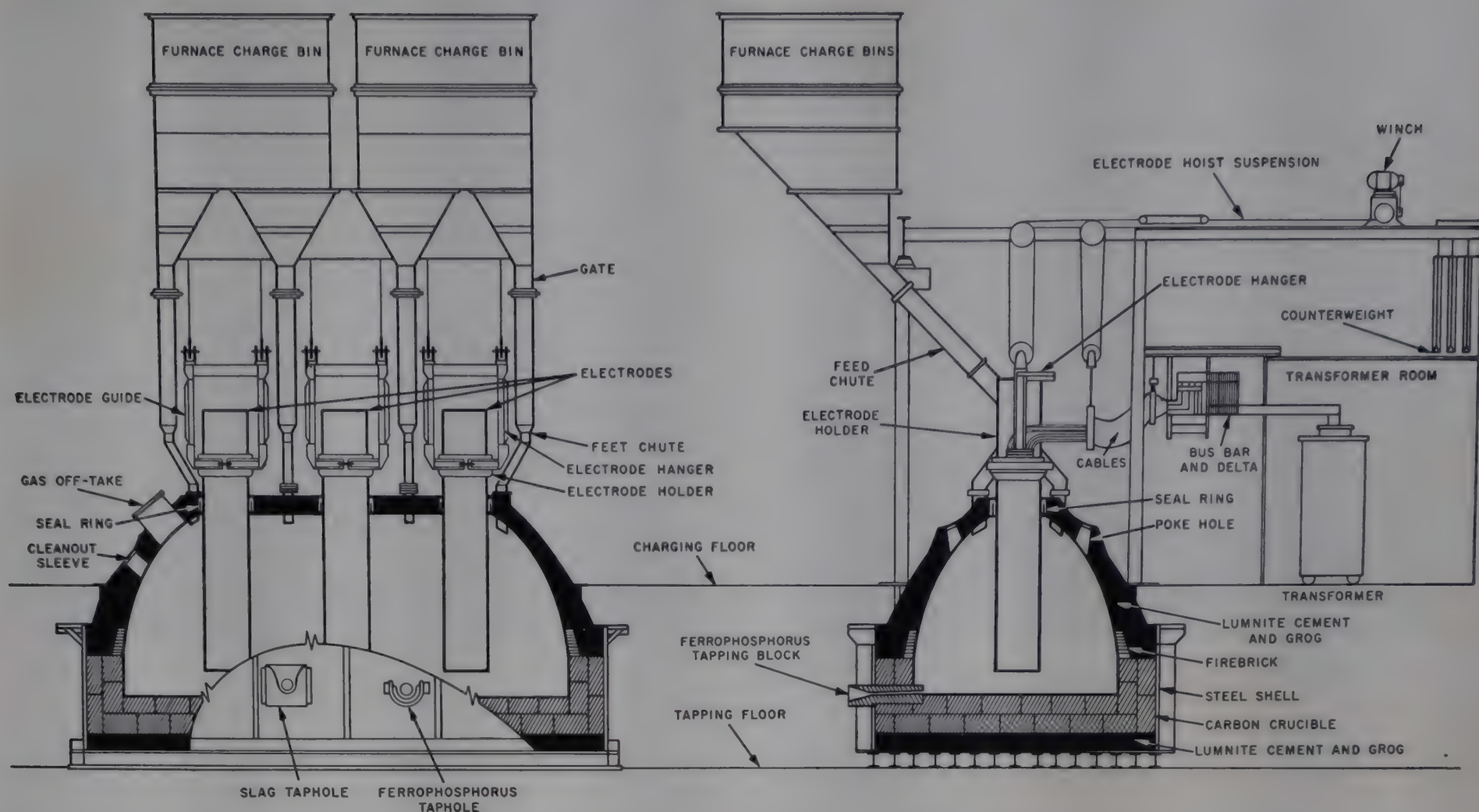
go to the proportioning building. Here, weigh feeders proportion the three furnace feed materials in correct amounts to a common conveyor leading to storage bins, and these feed by gravity directly to the furnaces.

Off-gases from the furnaces, containing product phosphorus,

Phosphate Rock Reserves in United States

Millions of Long Tons

State	Reserves under Present Conditions		Reserves under Changed Conditions	
	Marketable product	P ₂ O ₅ content	Marketable product	P ₂ O ₅ content
Florida	2040	660	23,350	4392
Tennessee	85	15	5,398	1129
Western Field (Mont., Idaho, Wyo., Utah)	3000	870	20,000	5800



A typical furnace consists of a steel shell lined with carbon blocks and covered with a monolithic roof of Lumnite cement and grog. The $\frac{5}{8}$ -inch steel shell encloses the carbon crucible and lower edge of the arch. It is insulated from the hearth (bottom of the crucible) with 4 inches of refractory and a 6-inch layer of Lumnite cement and grog. The furnace's steel base plate rests on steel I beam joists supported by concrete sills. This permits air cooling of the furnace bottom. A ring of Type 304 stainless steel spray nozzles surrounds the steel shell at its upper edge to provide constant water cooling of the furnace wall. Furnaces are grounded to a chemical ground field outside the furnace building.

Carbon blocks for the crucible bottom— $1\frac{1}{2}$ feet thick and $2\frac{1}{2}$ feet wide—are laid across the furnace in two layers, giving a total bottom depth of 3 feet. Blocks are full furnace width at the center and are cut to fit the rounded ends. Crucible walls are formed by similar blocks (nominally 1 foot 3 inches by 2 feet 8 inches, cut to fit furnace shape) laid to a height of $2\frac{1}{2}$ feet above the inner bottom. Blocks are cemented in place with carbon paste. Ten course of super duty fire brick (6E) are laid around the top inner edge of the crucible, supposedly to provide insulation for the lower edge of the furnace roof, but probably a carry-over from the all-brick construction used 15 to 20 years ago.

carbon monoxide, and traces of other gases, get a two-pass treatment in electrostatic precipitators for dust removal. Off-gases then go to water coolers where elemental phosphorus is condensed, separated from the other gases, and pumped to storage. Overhead gases from the condenser, mainly carbon monoxide, serve as plant fuel. Slag, predominantly calcium silicates, and ferrophosphorus are tapped from the bottom of the furnace at regular intervals.

Processing details vary from producer to producer depending on such items as individual company experience, plant location, ore characteristics, and furnace design. Major processing differences are furnace design and agglomerating method used on phosphate shales.

Electric furnaces require a lump charge to provide a porous bed for release of product off-gases from the reaction zone deep in the furnace. Most of the phosphate as mined is unsuitable for furnace feed and must be agglomerated to proper size. A variety of processes has been developed: pelletizing, nodulizing, sintering, and briquetting.

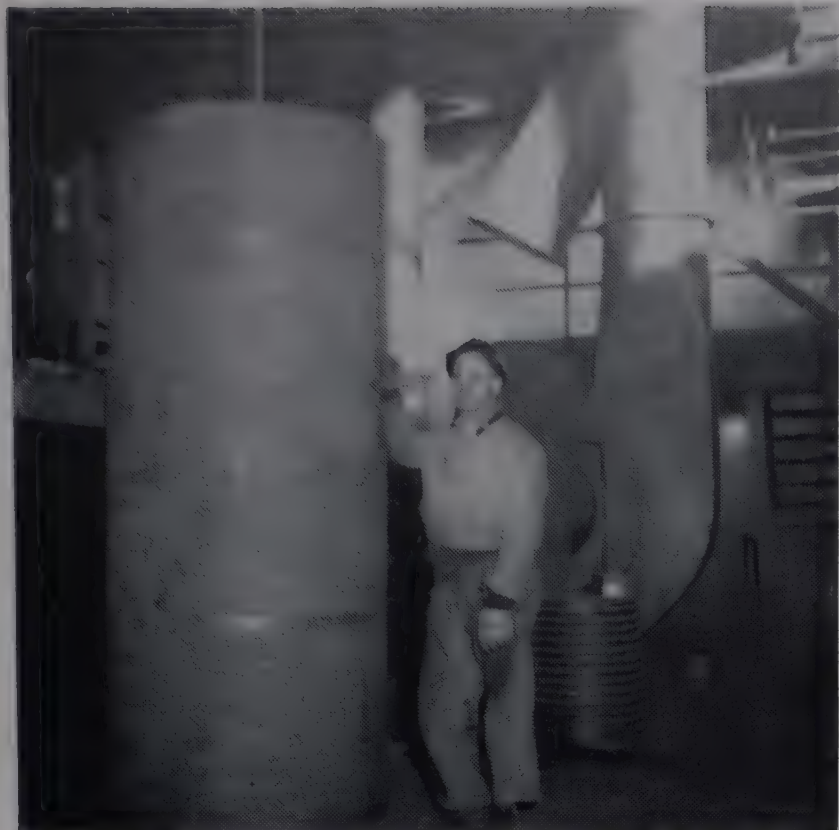
The furnace roof is a Lumnite cement and fire brick grog catenary arch. It is cast in place with provision for entrance of electrodes, feed chutes, poke holes, and product gas off-take pipe. The arch is about 2 feet 8 inches thick at the base and tapers to about 1 foot 6 inches at the top. The arch is designed as a structure to support furnace superstructure and to provide a gas-tight collection chamber for product off-gases.

Each furnace has six poke holes (furnace No. 4 has three), another carry-over from early furnace design, for use in dislodging build-ups and crusts. Westvaco seldom uses these in normal operation.

Each furnace has two tap holes in the crucible, one for ferrophosphorus (bottom flush with crucible bottom) and one for slag (8 inches above crucible bottom). The slag tap hole assembly is a 30-inch-diameter carbon shroud into which a bronze, water-cooled tapping block is fitted. Inside the bronze tapping block is a smaller water-cooled bronze casting, commonly known as a "tapping monkey." This monkey has a $2\frac{1}{2}$ -inch hole which controls slag flow during tapping. It is closed with a wooden stopper on completion of tapping. The ferrophosphorus tapping hole is a 30-inch-diameter graphite tapping block with a 3-inch tapping hole.

In pelletizing, phosphate fines are plasticized with water (and a clay binder, if needed), and moistened shale is tumbled into pellet shape in rotating drums. Pellets are then hardened by drying or calcining. In nodulizing, fines are heated in rotary kilns to incipient fusion, at which temperature they cohere and agglomerate. Sintering is accomplished by mixing fines with coal or coke and then burning the fuel from the mixture to fuse nonvolatiles in a mass. This mass is then crushed for furnace feed. Finally, in briquetting, fines are plasticized with water and clay binder as needed and then molded in a roll press. Briquettes are then dried or calcined.

Choice of agglomerating method depends on chemical and physical characteristics of the fines. Westvaco and Oldbury both pelletize and calcine. Monsanto pelletizes at its western operation and sinters in Tennessee, while Victor sinters at all three of its plants. Shea nodulizes, and Virginia-Carolina and American Agricultural Chemical are able to use mine-run material entirely.



Furnace electrode. Connections made with screw for top and bottom at right

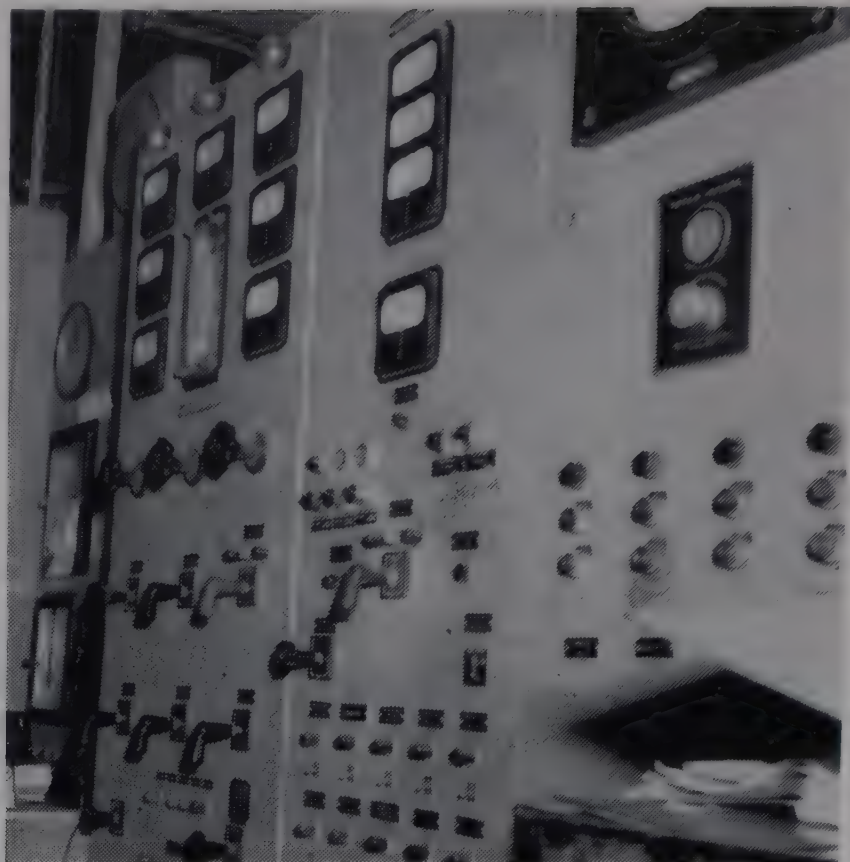
Two conventional furnace designs are used in the Westvaco plant. Furnaces No. 1, 2, and 3 follow TVA furnace No. 6 design—oblong with rounded ends and three in-line electrodes. Furnace No. 4, newest in the Westvaco line and believed to be the largest elemental phosphorus furnace now operating, is of Westvaco design—round with electrodes in a delta configuration. The drawing on the opposite page shows a typical oblong furnace similar to Westvaco's No. 1, 2, and 3 furnaces.

Located above each furnace are its feed bins—two for each furnace designed to hold a 32-hour supply. Four feed chutes of 16-inch diameter lead down to each of the TVA type furnaces. A two-way split in each chute places four chutes of 12 inches diameter around each electrode. Feed chutes do not protrude into the furnace proper, as flow characteristics of the burden cause it to assume the proper profile in the furnace.

In addition to these regular feed chutes, four fast feed chutes lead to each furnace directly from its storage bin. These are normally closed and are used to correct furnace burden as needed by improper proportioning.

Graphite electrodes (18E) are 35 inches in diameter and 108 inches long. They are in constant vertical motion to compensate for changes in furnace operating conditions. Therefore, electrodes are supported individually by automatically controlled arrangements of cables and sheaves. Each electrode holder consists of four water-cooled copper castings held in contact with the electrode by a steel band. Eight 2½-inch heavy wall copper tubes which supply both current and cooling water to the holders are connected directly to the holder. These tubes are supported at their outer ends by a cable and sheave system which moves in conjunction with that for the electrode holder. Water-cooled, flexible copper cables of Westvaco design connect these tubes to the bus bar for each furnace.

Upper and lower limit switches restrict electrode holder travel in the guide to 6 feet. Movement of electrodes is controlled automatically to a set kilowatt load (30E). This system consists of a generator supplying current to a direct current electric motor which raises or lowers the electrode. The generator is tapped across two voltages in the electrode system, one of which is proportional to current flowing in the electrode, the other of which is proportional to the voltage drop between electrode and ground. These voltages act opposite to each other in the generator, and current fed to the direct current motor causes it to raise or lower the electrode depending on which of the two voltages is greater.



Control panel operating No. 3 and 4 furnaces

Electrode position is therefore controlled by resistance of the furnace charge between electrode tip and ground. A decrease in this resistance, for instance, causes the electrode to rise to maintain a constant kilowatt load on the furnace.

A seal around the electrode allows it to move and prevents escape of product gases. The electrode rides against a water-cooled copper seal ring which is held to the furnace roof by a cast iron gland casting. Asbestos rope packed into the annular space between seal ring and electrode is held in place by a ring tightener.

Temperature gradient in the furnace varies from about 1450° C. in the slag and ferrophosphorus layers to about 300° C. at the top of the furnace burden. Major part of the phosphate reduction—probably 95 to 99%—takes place in the 1250° C.-to-arc temperature region which lies roughly between 1 and 3 feet from the inner bottom. Here, ore melting, reaction, and reduction begin as the melting phosphate comes in intimate contact with coke and silica. Balance of the reduction takes place in the upper slag layer as the melting ore flows toward the furnace bottom. Part of the reduction also takes place in burden layers immediately above the major reaction zone as product gases percolate up through the furnace burden.

As mentioned, Westvaco's first furnaces were oblong; the newest furnace is round and also larger. This conversion from small to large and from rectangular to round is typical of the trend in furnace design. However, factors in favor of either design indicate that choice of size and shape may be left somewhat to the discretion of the builder, with regard to characteristics of raw materials available.

In general, volume of phosphorus produced is directly proportional to kilowatt hours consumed in the furnace, assuming a given analysis of material charged. Although the industry has been reluctant to publish statistics or design data, results of actual operation of TVA furnaces published in the literature and TVA publications indicate the relative magnitude of this ratio.

Once a prospective furnace builder has decided on the volume of phosphorus to be produced and, thus, the kilowatt hours required, then the power load or rated capacity of the furnace or furnaces can be determined. Choice between several small furnaces or one large furnace depends upon the advantages of flexibility in operating small furnaces with contingent large fixed costs as contrasted with economics of a large furnace with lower capital and operating costs and higher thermal and material efficiencies.

Factors in furnace design. . .

To determine optimum voltage or voltage range, consideration must be given to the relationship of voltage-ampere ratio to the power load, electrode size, and number of transformer taps that make possible variation in load. Evidence has been accumulating that for given size furnaces an optimum relation exists between secondary phase voltage (I) and amperes per phase (E). This relation is, however, entirely empirical, varies with furnace conformation, feed preparation, and burden profile for given operating conditions and is controlled in some cases by availability of larger sized electrodes. Reported satisfactory operation has been achieved with I/E ratios from 80 to 173.

When power load is fixed for a determined production, a voltage increase causes electrodes to ride higher in the furnace. Up to a point, this may be advantageous in that deterioration to the carbon crucible (bottom and side walls) may decrease. On the other hand, if voltage is increased excessively, electrodes may ride sufficiently high to raise the dust load and temperature in the furnace gas above the practical limit for effective operation of the furnace, precipitator, and auxiliary equipment. Furnace off-gas temperatures of over 500° C. are intolerable. This might be overcome by increasing the depth of the furnace proper. However, limitations are soon reached in practical construction, electrode length, and heat transfer control in the burden. The additional and serious operating problem of tapping cold, viscous slag is invariably encountered when using high voltage without compensating high kilowatt load.

Lowering the voltage, while an apparent answer to operating difficulties, also has economic limitations. Low voltage for a given power load results in electrodes riding deep in the furnace, causing severe attack on the carbon lining. Since replacement of this lining is expensive and requires a lengthy furnace outage with serious production losses, frequency and cost of carbon lining replacement must be considered in determining design voltage.

Electrode consumption, a major item in the cost of phosphorus, is a second important factor in voltage selection. For a given power load, a lower voltage results in higher phase amperage. Empirical relations indicate electrode consumption varies as the current density increases, rising approximately as the ratio of the square of the current density after passing an optimum value. Increasing the electrode size reduces current density. However, limitations in electrode manufacture and in availability of commercial sizes restrict this area of design.

The fourth interrelated variable, voltage range of the transformer, is best determined by the capital cost of the transformer, as transformer costs rise rapidly with the number of voltage tap settings. Terms of the power contract for firm, interruptible, and dump power also must be considered.

The industry considers that optimum voltage ranges from 300 to 350 volts for furnaces having capacities of 9000 to 15,000 kw. to over 500 volts for larger furnaces of 40,000 kw.

Design of current carrying facilities and transformer is largely one of applying well known principles to obtain a high power factor and electrical efficiency. A high power factor circuit for the elemental phosphorus furnace is an economic necessity. A low power factor results in a high voltage drop between transformer and electrode tip, thereby reducing power in the smelting zone and increasing the ratio of electrical losses to usable power for a given current value.

To obtain a high power factor, one must consider applied voltage, current, circuit resistance, and inductive reactance of the furnace circuit. Of these, inductive reactance receives the most consideration when designing for high power factor, because it is a fixed value determined by geometry of the furnace circuit and the electrical frequency.

Resistance of fixed circuit components is a function of conductor length and section area, and it can be reduced to a very small value depending on economic limitations of initial cost *vs.* permissible power loss. On the other hand, inductance is a function of not only size and shape of the conductors but the actual physical relationship as well. Once the physical size and arrangement of the circuit conductors have been determined, the power factor then becomes a function of the relationship between current and voltage magnitudes. As the ratio of applied voltage to the circuit current is increased, the phase displacement between voltage and current is reduced and the power factor increases.

Circuit components considered when designing for power factor are inherent reactance of the transformer, fixed secondary bus, flexible conductors between fixed bus and electrode holder assembly, conductors connecting flexibles to electrode holder, electrode holder, electrode diameter and length, and assumed paths of current to the hearth.

A considerable latitude exists for the selection and design of various components up to the electrodes. However, despite the fact that the greatest percentage of reactance occurs in the electrodes themselves, other factors such as spacing, physical size, and arrangement limit the extent to which electrode reactance can be reduced. These factors must be considered for other reasons also, some of which have already been discussed.

Small diameter electrodes arranged symmetrically (equilateral triangle) with extremely close spacing approximates the ideal for low reactance. But current density and resultant electrode consumption determines diameter, and electrode arrangement depends on other physical components of the furnace. Besides physical problems associated with the furnace, electrode spacing depends on voltage between electrodes. Too close a spacing results in voltage gradients above the resistance of the furnace charge in the region above the reaction zone. As a result, current flow becomes uncontrolled in undesirable regions of the furnace, and control of electrode position in such a furnace would be impossible. Maximum electrode spacing is reached when the zones between electrodes become unreactive, stock bridging occurs, and tapping becomes impossible.

To select physical size of the furnace, the following must be balanced: hearth area as governed by furnace load, horizontal hearth dimensions as controlled by electrode size, secondary voltage, feed characteristics, and burden profile. The usual measure of hearth area is kilowatts per square feet. Because of the effect on I/E of materials used, there are no established data for this factor. Successful operation has been attained from 20 to 60 kilowatts per square foot with various I/E and material combinations. When the kilowatts per square foot of hearth area exceed the maximum energy absorption limits of the furnace charge, local overheating causes abnormalities in furnace operation and raises possibilities of premature hearth failure. However, the energy applied should be sufficient to maintain the slag molten and at reactive temperatures over the entire hearth area.

Furnace depth is a function of heat transfer from the gases generated deep in the furnace to the incoming stock, so that off-gases are above the phosphorus dew point but below temperatures affecting equipment and its operation. The ideal off-gas temperature falls around 300° C. Thus, heat transfer in the furnace must be sufficient to cool reaction gases from perhaps 6000° C. at the electrode tip to 300° C. Heat transfer depends on burden size and size distribution, permeability as it rests in the furnace, fusion temperature, and the like. Such factors must be known, as well as the normal distance of the electrode tip from the hearth, before optimum furnace depth can be calculated.

After the total power load per furnace has been established, the electrical variables of voltage, amperage, and power factor can be determined. Data covering relationships among these variables are very meager, and calculations are based on experience.

Figure 1 is a flow sheet for the process. Phosphate shale for the Westvaco plant comes from a strip mine 27 rail miles distant operated by J. R. Simplot Co. on long term lease from Fort Hall Indian Reservation. The phosphoria formation at the Fort Hall mine is approximately horizontal and lies under 20 to 150 feet of overburden. It consists of an upper layer of phosphate shale 10 to 30 feet thick of about 25% phosphorus pentoxide separated by a limestone layer from the lower layer of phosphate rock 6 to 8 feet thick of 30 to 32% phosphorus pentoxide.

Simplot opened the mine in 1946, and prior to Westvaco's advent on the scene, it stripped and stockpiled the low grade shale and used the high grade rock for phosphate fertilizer manufacture at its Pocatello plant. Westvaco began buying ore from Simplot in 1948. In addition, it has its own reserves on the Fort Hall reservation and in the Crawford Mountain area of north-eastern Utah.



Shale is discharged from hopper cars by bottom dumping directly to a hopper located under Westvaco's siding. Since ore is not entirely free flowing, a car shaker (9E) is used. Cars, each containing 60 tons, are unloaded at a rate of 30 to 40 cars per 8-hour shift.

An inclined conveyor carries shale from an apron feeder under the track hopper to a conveyor transfer house. Here it is again sampled, and it may be sent to storage or directly to process over a 365-foot inclined conveyor to the top of the pelletizing building. Shale as mined is nonuniform from car to car, varying from 22.5 to 27% phosphorus pentoxide, 33 to 38% calcium oxide, and 20 to 30% silicon dioxide. Mixing during unloading, stockpiling, pile trimming, and reclaiming gives a more uniform feed to the plant. Therefore, all shale proceeds directly to the stockpile.

Shale is reclaimed from the stockpile by bulldozers and a 4-yard Scoopmobile. The latter is a recent addition to reduce production of fines during shale handling. The Scoopmobile is an oversize front-end loader that scoops and carries its load in contrast to bulldozers which push and thereby break some of the lump. Bulldozers and Scoopmobile discharge to a 10-yard movable hopper located in a 20-by-40-foot tunnel.

During winter, shale freezes in the pile, bins, or other stopping points. The recovery system is designed to keep shale moving at all times until it arrives at a process stage where heat is supplied. Shale in the reclaiming hopper discharges directly to an inclined conveyor running to the conveyor transfer house, where it changes to the belt conveyor running to the top of the pelletizing building.

Phosphate shale is mined by conventional stripping methods. The mine location—at an elevation of 5600 feet at the base of

Mount Putnam, one of the highest peaks in the Blackfoot range—limits actual mining to the period from May 1 to September 30. During several weeks before and after this season, stripping overburden, road relocation and improvement, and other preparations are made as weather permits for expeditious mining of ore blocked out for the following season.

The phosphate shale, a sedimentary deposit, was laid down in relatively thin layers $\frac{1}{4}$ to 4 inches thick. These laminations are separated by parting layers of fine phosphatic clay. Shale in place is relatively soft, and normally no blasting is required. Once the overburden is stripped, high capacity Diesel shovels scoop the ore into trucks which carry it to hopper car-loading facilities where it is crushed and sampled.

Union Pacific owns and operates a 22-mile spur from the mine to its main east-west line. This was constructed specifically for movement of phosphate to the Westvaco and Simplot plants near Pocatello. Shale discharged from hopper cars into a hopper goes onto an inclined conveyor.

At the discharge of the inclined conveyor, shale is sized in a 5-by-12-foot double deck screen (24E) having $2\frac{1}{2}$ inch square holes in the top deck, $\frac{1}{4}$ -by-5-inch slots in the bottom. Plus $2\frac{1}{2}$ -inch material from the top deck discharges into a 50 hp. hammer mill (11E) to reduce maximum size to 2 inches.

Crushed shale is carried by 24-inch rubber belt conveyor to one of eight storage bins (steel, 240 tons usable capacity each). Undersize, or phosphate fines, from the screen moves by 24-inch conveyor to one of the same eight storage bins. During winter months, this storage is by-passed, and fines are conveyed directly to the pellet plant.

Phosphate fines are agglomerated into pellets of plus $\frac{1}{4}$ inch, minus 2 inches. Westvaco accomplishes this in a four-step pelletizing operation consisting of mixing with water in pug mills; further mixing and extruding in mullers; pelletizing agglomerated material in rotating drums; and drying these pellets in conveyor dryers.

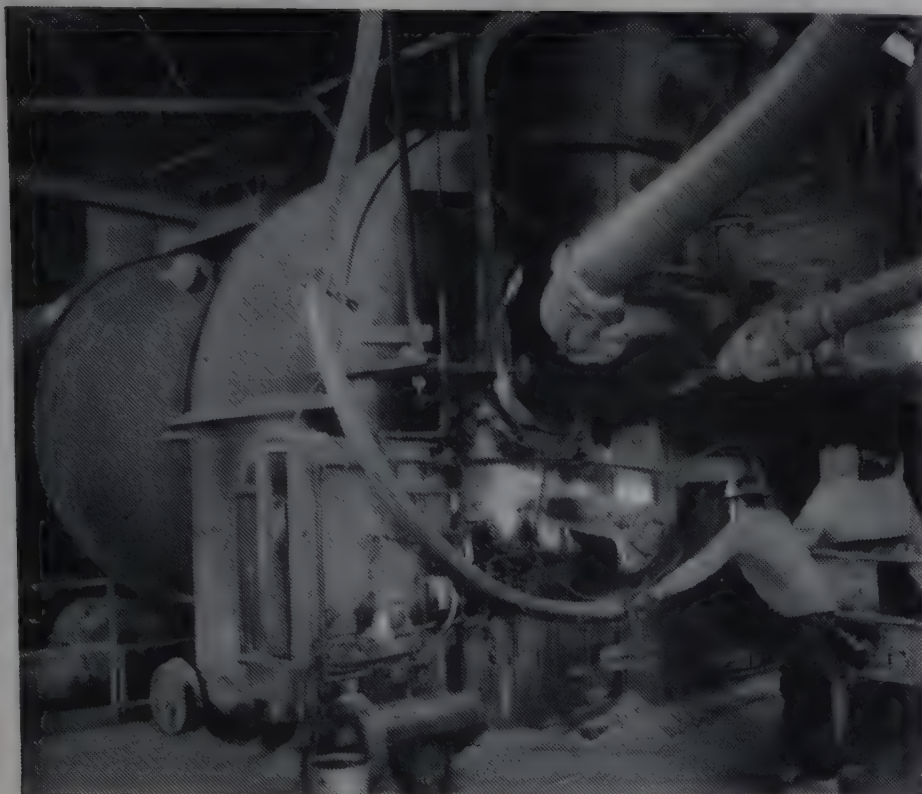
The muller feed bin has a capacity of 120 tons. Spacers in the bin direct phosphate fines to feed chutes located on each of the four corners, and constant volume apron feeders 10 feet long carry material directly to each of the four pug mills (20E). Pug mills are provided with jackets for steam heating during winter, but need for heating is infrequent.

Water is added manually to shale in the pug mill, and two counter-rotating shafts with closely spaced paddles blend the shale and water. Each pug mill discharges directly to its associated muller. The mix at this point can be formed into stiff mud balls by hand. Mullers (19E) further mix, knead, and grind the feed; deaerate it; and partially preform pellets by extruding blended shale through holes in the muller pans at their discharge areas.

The muller bowl is about 12 feet in diameter. Two wheels weighing about 2 tons each ride each side of the arm which turns at 18 r.p.m. A series of spray nozzles permits more water to be added manually to the mix in the mullers for final plasticity adjustment. Scrapers direct shale through two circuits of the bowl before it arrives at the discharge area. Here, it is extruded through about 750 holes $1\frac{1}{2}$ inches in diameter to a conveyor below which carries extruded material to the pelletizer.

Pelletizing requires a feed which will roll and cohere. Because of variations in size and water content of the feed, exact moisture specifications cannot be set, and automatic controls cannot be applied. Water addition, therefore, is more of an art than a science. The operator watches products from the muller and pelletizer and adds water accordingly. If there is an excess of undersized pellets, for instance, more water is added.

Extruded shale from the mullers is conveyed to the pelletizer. This is a steel drum 11 feet in diameter and 36 feet long, which rotates clockwise. A series of longitudinal angles protruding 1 inch into the drum lifts and rolls the feed as it moves through the drum. A burner fueled with by-product carbon monoxide ex-



Kilns (23E) are standard industrial units. Drive is by electric motor through one ring gear, and each unit has a stand-by Diesel engine for emergency drive in case of power failure. Firing is by fuel oil and by-product carbon monoxide from the phosphorus furnaces. Of the 2,000,000-plus B.t.u. required per ton of product, 60% is currently supplied by oil. Firing temperature is 1100° to 1200° C., the incipient fusion range of the material.

Since the material is at or near incipient fusion, minor variations in temperature result in formation of rings of semiplastic material in the hot zone of the kiln. Occasionally, large balls of semifused material collect behind these rings. A water-cooled boring bar is used to remove build-up in the final firing zone.



At the kiln inlet, pellets dry, and as they progress through the kiln the organics burn out. Final firing for calcining takes place in the last 40 feet.

Each kiln discharges to a cooler (5E) where average temperature of the calcined material is dropped to about 200° C. Ring removal results in a certain number of "balls and slabs" being formed. Those of large diameter are removed manually from a grating onto which material from the cooler discharge and are carried to a separate room where they are allowed to cool before being returned to the system for crushing (slabs of this size are in a plastic, semifused state in the center and cannot be crushed until cool).

tends the full length of the pelletizer close to the inner surface (at about 2 o'clock when viewed from the discharge end). Heat provided warms the surface of the drum and reduces sticking.

Fitted at the end of the pelletizer is a trommel screen section which segregates under- and oversized pellets. Undersize material—minus $\frac{3}{8}$ inch—is removed in the first 6 feet of the trommel. Properly sized material—plus $\frac{3}{8}$ inch, minus 2 inches—is removed in the next 3 feet. Oversized material discharges over the end. Oversize and undersize are recycled to the pug mills.

Pellets, containing 13 to 14% moisture at this point, are too wet for feeding directly to kilns for calcining, and they are dried first to less than 4% moisture in two continuous conveyor dryers (21E). The dryer chamber is an insulated steel shell 8½ feet by 10 feet in cross section and 84 feet long. The belt is 7½ feet wide and consists of perforated steel plate sections 1 by 7 feet with $\frac{3}{16}$ -inch perforations. It moves at 3 feet per minute.

Hot air for each dryer is supplied by a separate furnace (2E). The furnace provides about 23,000,000 B.t.u. per hour of 200° C. air. The lower chamber of the dryer is baffled for heat distribution, and the upper section is equipped with dampered outlet ducts. Exhaust air is handled and the system pressures controlled by a 150-hp. exhaust fan (3E).

Pellets are distributed at a uniform depth on the dryer belt by a company-designed modification of a conventional belt feeder (13E). Pellets reach about 150° C. Dried pellets from both dryers are conveyed by 24-inch belt conveyor to a 3-by-5-foot screen (26E) having $\frac{1}{4}$ -inch openings. Here, they get a final sizing before being fed to the kilns for drying, burning of organics and calcining. Fines, recycled to the raw shale storage bins, are returned to the pelletizing system.

Most of the kiln product passes through the cooler grating to a live roll grizzly (22E) having nine rolls on 3-inch spacings. Plus 3-inch material discharges from the end of the grizzly to a double

roll crusher (7E). Feed is crushed to minus 3 inches, recycled to the cooler, and recombined with kiln discharge.

Material passing through the grizzly is conveyed to a 3-by-10-foot double deck screen (26E) having 0.375-inch square openings at top and 0.145-inch square openings at bottom. Provision is made on the conveyor to this screen for material to be diverted to outside storage. Only a minimum amount is diverted, however, to serve as make-up feed during kiln outages.

Undersized fines from the screen are carried from the screen by elevator to a fines storage silo and added to raw shale entering the pellet plant. Screened calcine is carried by 24-inch conveyor to the proportioning building and stored in five storage bins of 400 tons usable capacity each. Screened nodules represent about 80% of the total furnace charge.

To reduce atmospheric pollution and improve plant and area working conditions, Westvaco takes dust-laden gas streams from each kiln and pulls them by induced draft fan at a rate of 160,000 cubic feet per minute through a 196-tube cyclone separator (29E). Some 50,000 tons of dust per year are collected by the separators and recycled with phosphate fines to the pelletizing plant.

Kiln gases then pass through Westvaco-designed wet scrubbers. Particulate matter discharged is reduced to less than 200 pounds and undesirable gaseous material to 5 pounds per day per kiln.

Second major material for furnace burden is coke. Coke specifications call for a material having high reactivity (carbon content greater than 85%), a reasonable amount of physical stability, and proper size. Westvaco uses both beehive and by-product coke purchased from western steel mills. Specifications are fixed carbon 86.0%, moisture 2% maximum, 95% minus $\frac{5}{8}$ inch, and 95% plus 6 mesh for coke purchased as "sized and dried." This amounts to about 50% of the coke used; the balance must be processed by Westvaco.

A coke stockpile is operated on a 90-day minimum, and coke is

sent directly to process 80% of the time as cars are received. It is received on a year-round basis.

Coke for sizing and drying is discharged from rail cars to the coke hopper (or reclaimed from the stockpile by Scoopmobile and dumped into this hopper) and conveyed by pan conveyor and continuous bucket elevator to an enclosed, vibrating screen (25E) 4 by 8 feet, double deck, 2 $\frac{1}{2}$ -inch square openings at top, $\frac{1}{8}$ -by-3 $\frac{1}{2}$ -inch slots at bottom. Oversize coke from this screen goes to a roll crusher (12E) of 15-tons-per-hour capacity. Size is reduced to minus $\frac{3}{4}$ inch, and it is returned to the screen. Undersize (coke fines) amounts to about 11% of the feed; this is stockpiled in outside storage for sale.

Properly sized coke—minus $\frac{3}{4}$ inch, plus 6 mesh—is conveyed to one of two live storage silos (each having a 50-ton capacity) from which it is fed via constant volume feeder (8E) to a rotary shelf coke dryer (10E).

The dryer is 12 feet in diameter, 23 feet high, and has 14 trays. By-product carbon monoxide is the fuel used to provide 6,000,000 B.t.u. per hour at temperatures not to exceed 400° C. Feed to the dryer is 15 to 16 tons per hour, and it operates about 25% of the time to supply plant needs. Coke moisture is reduced from an average of 11% to less than 2%.

A cyclone separator (28E) containing 63 tubes removes coke fines from dryer gases. These fines, amounting to 4500 tons per year, are also sent to the coke fines stockpile for sale.

Dried coke is conveyed and elevated to the top floor of the proportioning building to an electrically-vibrated, inclined screen (25E), 4 by 8 feet with $\frac{1}{4}$ -by-3-inch slots in the top deck and 0.125 inch square openings in the bottom deck. About 10% of the coke feed is removed as fines at this point. These are also sent to the coke fines stockpile for sale. Counting moisture and fines removed, about 75% of the raw feed remains for use in the furnaces. The properly sized coke is stored in six bins in the proportioning building (three of 156-ton capacity, and three of 78-ton capacity).

Silica, third furnace burden material, is mined in a nearby quarry owned by Westvaco. Chemically, silica acts as a flux in the furnace and, therefore, should be high in silicon dioxide. In general, impurities in the fluxing material reduce its effectiveness and dilute the total furnace burden. This results in lower phosphorus output per unit of energy used.

Physical requirement for silica is that it must melt smoothly and not shatter under furnace heat. If it shatters, the resulting smaller sized particles segregate to give an undesirable distribution of materials in the furnace burden.

Silica is mined during the May to September mining season (weather controls exact season length) and is trucked to the Westvaco plant. A 3-month minimum stockpile is maintained.

The only processing required is sizing. This is done at the quarry by crushing and screening to plus $\frac{1}{4}$ inch, minus 2 inches. Silica is reclaimed from the stockpile by mobile equipment and dumped into a 3-cubic-yard hopper. It is carried from the hopper by a belt feeder and elevated to the proportioning building where it is stored in a 275-ton-capacity bin.

Proportioning is probably the most critical single operation in elemental phosphorus manufacture. Proportioning bins are in two parallel lines—five nodule bins in one, six coke and one silica in the other. Located on tracks beneath these bins are five moving belt weigh feeders (14E), two for nodules, two for coke, and one for silica. These feeders operate at right angles to the bin lines and discharge toward the center to a common, 30-inch belt conveyor which runs between the bins and carries proportioned material to furnace storage bins located above each furnace. Capacity range of feeders is 21.4 to 128.4 tons per hour. At any given time, one or more nodule, one coke, and the silica storage bin are discharging simultaneously.

As each proportioning storage bin is filled, it is sampled and the material analyzed. Analyses include fixed carbon, moisture, calcium oxide, silicon dioxide, ferric oxide, aluminum oxide, phosphorus



Slag is tapped on each furnace for 20 minutes every hour and flows via slag runner to one of two slag pits above associated with each furnace just outside the furnace building. Pits are alternated daily, one cooling and being emptied while the other is filling. Slag removed from the pits by a 2 $\frac{1}{2}$ -yard shovel is trucked to a slag stockpile. It is sold mainly for concrete aggregate and road material. A relatively small quantity goes into slag wool insulation. An analysis is illustrated on the following page.

Typical Analysis of Feed Materials

Analysis	%			
	Raw shale	Nodules	Coke	Silica
P ₂ O ₅	24.0	25.5		
CaO	36.6	38.8		1.0
SiO ₂	23.3	25.1		92.2
Al ₂ O ₃	6.5	6.8		4.5
Fe ₂ O ₃	1.8	1.8		1.3
F ₂	2.0	1.8		
V ₂ O ₅	0.28	0.25		
Cr ₂ O ₃	0.23	0.20		
MnO ₂	0.12	0.13		
U ₃ O ₈	0.0008	0.0008		
C	3.0	0.2	86.5	
Volatile carbonaceous matter			1.8	
H ₂ O			1.1	
Ash			11.8	

pentoxide, and at times other components. From these analyses, the proper proportions of nodules, coke, and silica are calculated to form a mixed feed containing the precise amounts for effective reduction and melting in the furnaces. These proportions are converted by laboratory personnel to weigh feeder settings for each bin and used by proportioning plant personnel as feeding is started from each bin. Mixing of the furnace burden is accomplished by various transfers as the feed is conveyed to the furnace building. The table gives typical analyses of three feed materials.

Westvaco purchases three phase power from Idaho Power Co. Power arrives at 138,000 volts at the utility company's substation near the Westvaco plant, where it is reduced to 13,500 volts and distributed to each furnace transformer. Westvaco is the largest single customer of the utility company, and Idaho Power Co. is augmenting its power supply with interchange purchases from Utah Power Co.

The four Westvaco furnaces are located in a building about 90 by 400 feet, 92 feet high. Associated with each furnace are overhead feed bins, a transformer, a two-stage electrostatic precipitator, a condenser, a sump for product phosphorus, and a



Slag is tapped 45 minutes each 24 hours into chill molds (pigs of 3 to 5 tons each), carried to storage, and crushed. It is sold to steel companies for use as an alloying agent. Analyses of by-product are shown

Typical By-product Analyses

Analysis	Slag	% Ferro-phosphorus	Precipitator dust
P ₄		27.1	
P ₂ O ₅	1.0		38.4
K ₂ O			13.7
CaO	48.2		16.3
SiO ₂	38.3	0.15 ^a	19.6
Al ₂ O ₃	5.9		
Fe ₂ O ₃	0.14		
Fe		59.2	
F ₂	2.6		1.1
Cr		4.5	
V		5.4	
Ni		0.74	
Mn		0.51	
C			1.6

^a As silicon.

blower system for furnace pressure control and for handling carbon monoxide from the furnace system to the various points of use.

Furnace burden is conveyed the length of the furnace building from the proportioning building and diverted by tripper to furnace storage bins.

Furnaces operate under slight pressure—0.05 to 1.5 inches of water—to prevent entrance of air. Once started, they run continuously and automatically, with major duties for operators being slag and ferrophosphorus tapping, assuring feed is continuous and proper, changing electrodes as they are consumed, and continuously checking conditions throughout the units.

Burden feeds continuously to the furnace by gravity from the overhead feed bins. As slag and ferrophosphorus are tapped from the bottom and product gases exit, the burden gradually works its way down through the furnace, and fresh burden flows in at the top.

Furnace off-gases exit between 200° and 400° C. (this is the permissible range; Westvaco is presently controlling exit temperature at 300° C.). Off-gases contain:

Compound	Volume, %
Carbon monoxide	85.35
Phosphorus (P ₄)	8.42
Methane	1.24
Ethylene	1.00
Hydrogen	3.00
Silicon fluoride (SiF ₄)	0.51
Carbon dioxide	0.48

Final processing steps consist of removing entrained solids, condensing elemental phosphorus to separate it from other off-gases, and then holding the phosphorus just above its melting point for transferal to storage and shipment.

Off-gas is cleaned by electrostatic precipitation of entrained dust. Each unit (27E) consists of essentially two precipitators operating in series with necessary ducts so that flow of gas is up and collected dust is down. Each unit has facilities to provide or remove heat to maintain gases at about 300° C. Gas flow is 2.5 feet per second, and each pass removes about 95% of entrained dust in gases entering the pass.

Dust contains fly dust from the furnace charge and such volatiles as potash, soda, some rare earths in minor quantity, and any anhydrous phosphorus pentoxide that may be formed in the system by air leakage or occlusion in the feed. Collected dust is dumped into air-tight hoppers about every 4 hours and then into gas-purged containers where it is slurried with water to prevent spontaneous combustion. The material is dried and sometimes sold as fertilizer.

Dust-free product gases exit from the second pass precipitator and move by 30-inch pipe to the condenser, a cylindrical column 5 feet in diameter and 33 feet high. Two rings of sprays in the condenser, one at the 13-foot level and one at the 17-foot level, inject enough water to cool the stream to 55° to 60° C. (amount of water varies with furnace production; it is about 400 gallons per minute per condenser). Objective in condensing is to get phosphorus as close to its freezing point as possible without actually solidifying it, thus removing the maximum from the gas stream.

Once condensed, all phosphorus must be handled under water. Condensed liquid phosphorus flows down through the condenser and via 4-inch pipe to underground phosphorus sumps for each furnace. These rectangular concrete tanks are divided into collection and separation compartments. Each sump holds the production of about one day.

Phosphorus is pumped by a special heavy duty pump (4E) at a 55-gallon-per-minute rate once daily from each sump to storage—five above-ground tanks of 250,000-pound capacity each. These are insulated with 4 inches of asbestos, and steam coils maintain contents at 55° C.

Prior to introduction of phosphorus to the storage tanks, it is filtered in a porous tube filter (1E) having 12 tubes and 42 square feet of filter area. This removes any traces of precipitator dust or other solids from the final product.

Overhead gases from the condenser, consisting mainly of carbon monoxide, are pumped (17E) through an entrainment separator and then used as plant fuel. Since carbon monoxide output varies from hour to hour, only that part below the expected minimum is used as plant fuel. Carbon monoxide in excess of this is flared.

The life of a furnace lining is governed by the duty imposed on it, and the plant manager of any phosphorus plant must balance production rates and production procedures against lining replacement cost. Lining replacement includes not only direct repair costs but also loss of production during the 40-odd days required for replacement and modernization of the unit. The design and

Instrumentation

Instrumentation in various forms plays a major role in economic production of elemental phosphorus. In general, most instrumentation in the Westvaco plant follows accepted industrial practice throughout for such items as boilers, hot air furnaces, kilns, automatic weighing, and various alarm systems. Furnace temperature and pressure are two of the more novel instrument applications, however.

Temperature control of furnace off-gases is essential. Too high a temperature overheats auxiliary equipment and causes erratic operation; too low a temperature causes premature condensation of phosphorus, with resultant product losses and operational difficulties in precipitation equipment.

Temperature control is essentially a function of furnace operation techniques and design, since conditions inside the furnace determine ultimate temperature of gases leaving in the off-take pipe. Hence, instrumentation's major role in furnace temperature control is accurate determination of temperatures at various points along the gas route. Some measure of control is achieved, however, by auxiliary heating of precipitator shells with thermostatically controlled electric heating elements during periods of low gas temperatures.

Iron-constantan thermocouples are used as temperature sensing elements in the furnace system. Two multiple point strip chart recorders (15E) are used to indicate and record the most important temperature points, such as furnace off-take, precipitator inlet and outlet, and condenser inlet and outlet.

Because of the need to operate furnaces under a slight but controlled pressure, a furnace pressure system is vital. To perform successfully, the control system must maintain the slight positive pressure within narrow limits despite sudden and extreme pressure changes characteristic of elemental phosphorus furnace operation.

Control of furnace pressure is achieved by the position of two butterfly valves in by-pass lines around the compressor which pumps on overhead gases from the condenser. Furnace roof pressure is measured by an indicator-transmitter (16E) located near the furnace to reduce time lag. Its range is from 5 inches of water above to 5 inches of water below atmospheric pressure.

The indicator-transmitter signal goes to a receiver-controller located near the control valves and to a remote recorder-controller located in the furnace control room. The furnace room instrument is also connected to the receiver-controller at the valves through a manual loading line. This permits manual operation of the control valves when necessary.

The by-pass valves control pressure in the system by permitting gas to recycle around the compressor during periods of negative furnace pressure and allowing gas to be pumped from the system when excess pressure exists. The valves are adjusted to permit a slight gas recycling (feed-back) during stable operation as a means of keeping the system at the desired set point.

operation of phosphorus furnaces is still relatively a "black art." Therefore, major maintenance activity is "obsolescence control."

Procedures for major overhaul on furnaces are planned carefully in advance. Feed chute gates are closed first some time before scheduled shutdown. As the furnace continues to operate and slag and ferrophosphorus are tapped out, burden level gradually lowers. With less burden to move through, off-gases gradually increase in temperature. After some 24 hours, or when off-gas temperature reaches a point where damage to the effluent system is imminent (at about 500° C.), furnace current is

stopped. Ferrophosphorus and slag are drained as much as possible, and electrodes are then withdrawn to prevent their becoming frozen in the solidifying slag.

After furnace current is stopped, carbon monoxide is removed from furnace, precipitators, and condenser by a 2-hour purge with saturated, 110-pound steam.

The entire maintenance schedule requires 42 days. When maintenance is completed, the unit is turned back to the operators for test and preliminary operating work.

The carbon crucible is the critical part of the furnace. While the large blocks are prebaked, cement used to hold them in place is not carbonized. Therefore, joints must be carbonized in place and the whole hearth converted essentially to a single piece. Improper baking-in can result in slag or ferrophosphorus running through the joints and shell (tapout) to cause damages up to \$1,000,000 to furnace room equipment.

Electrodes are consumed gradually as the furnace operates. When the holder begins to approach the lower limit of its travel as the moving electrode compensates for changing furnace conditions and electrode usage, the electrode is suspended temporarily by an auxiliary crane located over the furnace and the holder slipped up to a new position.

(Text cont'd on page 14)

Maintenance

Maintenance of a phosphorus plant is one of the most important functions in plant organization. New employees are screened and old employees periodically checked on their skills by questionnaires designed to test their knowledge of plant operations.

Maintenance at the Westvaco plant varies from the routine application of a grease gun to the 40-day rehabilitation of a furnace. The major processing units are on a regular preventive maintenance and repair schedule, and emergency breakdown work is thereby kept at a minimum. The preventive schedule includes:

► **Stockpiling.** Shale cars are unloaded on a 6-day basis. The seventh day, Monday, is devoted to routine maintenance on stockpile conveying equipment, car unloading equipment, and associated bulldozers and shovels.

► **Pellet Plant.** The line is shut down 1 day each week for preventive maintenance throughout the line. Pug mill blades are rebuilt and hard surfaced during this time. Muller floor plates are replaced at 4-week intervals, and muller wheels are face surfaced by an automatic welder at about 3-month intervals. (The automatic welder is also used to hard tip hammer mill hammers, crusher rolls, pan conveyor rollers, heavy equipment shafting, and truck rollers for tractors and other crawler equipment. Except for machine fit work, the laid metal is smooth enough for use without surface finishing.)

► **Coke Sizing and Drying.** An outage is scheduled every 2 weeks. Screen cloth and crusher rolls are replaced and dryer flights repaired during this period as needed.

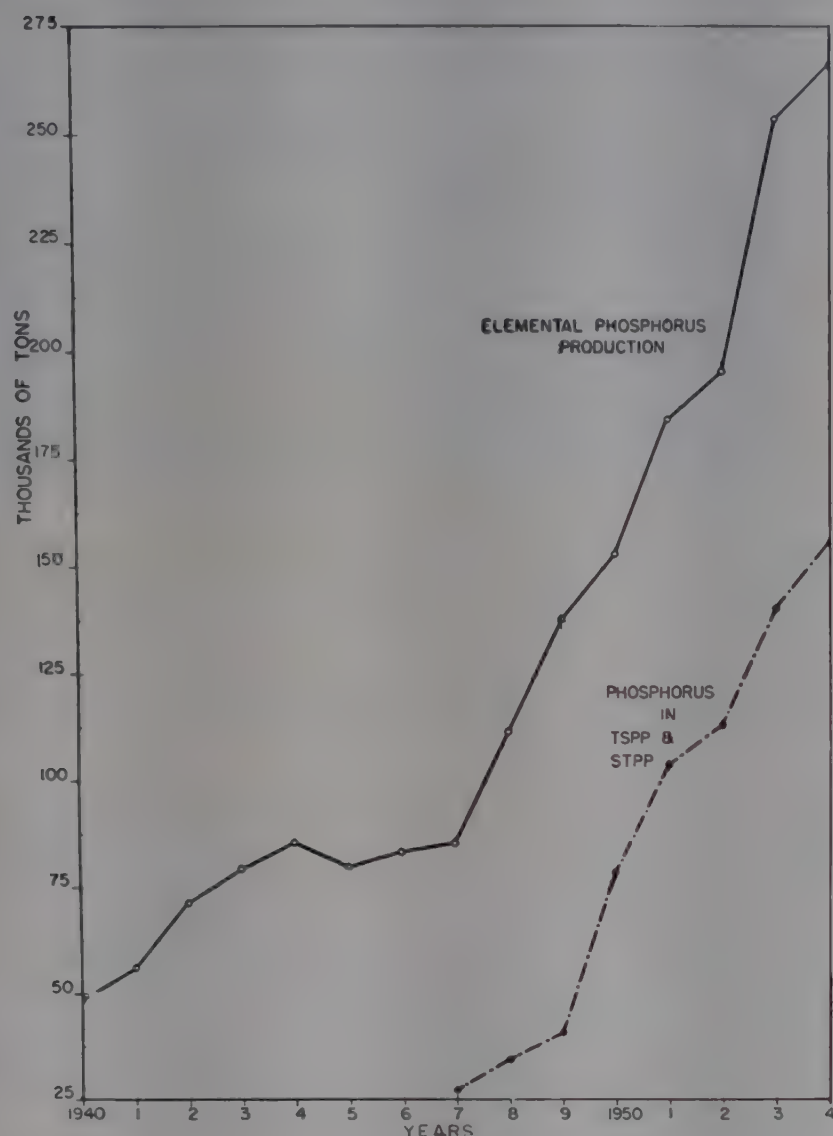
► **Proportioning.** Critical units in this section are weigh feeders. These are inspected, repaired, and calibrated daily.

► **Kilns.** Each kiln is shut down at 5-to-8-month intervals for brick lining repair where necessary. About 3 or 4 days are required.

► **Precipitators.** Each furnace is shut off for 1 to 3 days every 4 months for inspection, clean up, and repair of precipitators. Wires and frames are straightened, and weights on precipitator wires are replaced as needed. On each routine furnace outage for electrode replacement or holder slipping, all insulators on the 60,000-volt half-wave system are cleaned to prevent arc-overs.

What are the trends?

Since 1947 an increasing percentage of the phosphorus produced has found its way into synthetic detergents by way of sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP) as shown in the figure. However, an unknown per cent of these phosphates is made from wet process phosphoric acid, so that the curve showing phosphorus in these compounds does not represent elemental phosphorus in their manufacture.



Thousands of Tons

	TSPP		STPP		P ₄ in STPP and TSPP	P ₄ Pro- duction
	M Tons	P ₄ Equiv. ^a	M Tons	P ₄ Equiv. ^a		
1947	56.6	13.2	55.5 ^b	14.0	27.2	85.9
1948	66.4	15.5	74.5 ^a	18.8	34.3	112.0
1949	78.4	18.3	91.5 ^b	23.1	41.4	138.0
1950	85.7	20.0	233.0	58.8	78.8	153.0
1951	86.4	20.1	331.5	83.7	103.8	184.7
1952	84.8	19.7	370.0	93.4	113.1	195.1
1953	95.3	22.2	468.0	118.2	140.4	253.7
1954	107.0	24.9	518.7	131.0	155.9	266.9

^a Conversion factors to P₄ equivalent—TSPP, 0.233 and STPP, 0.2525.

^b Estimated.

The dependency of increased phosphorus production on the increased use of phosphates in syndets is apparent and any projection of phosphorus production must take this into consideration. The growth of syndets has been spectacular and in 1954 they represented 58.0% of the total of soaps and synthetic detergents sold. It is believed that syndets will eventually constitute 70 to 75% of all soaps and detergents sold (2) and that by 1960 this figure could be 65%. Sales of all soaps and detergents have increased at the rate of 1.7% for the last 30 years, so using

the 1954 figure of 2,037,000 tons the total projected for 1960 is 2,270,000 tons. Multiplying this figure by the estimated percentage of syndets, 65, gives 1,460,000 tons. For five years the ratio of tetrasodium pyrophosphate plus sodium tripolyphosphate production to syndets sales has averaged 52.7%. If this continues through 1960 and if tetrasodium pyrophosphate continues to represent 17.3% of the combined tetrasodium pyrophosphate plus sodium pyrophosphate, the average figure for the last two years, the total phosphorus consumed in syndets in 1960 will be 192,000 tons, an increase of only 37,400 tons above 1954. Thus it appears that the increase in phosphorus production due to phosphates used in syndets will taper off rapidly from this point on.

Sales—Soaps and Synthetic Detergents

Thousands of Tons

	Soaps and Detergents ^a	Synthetic Detergents ^a
1947	2031.0	200.0
1948	1884.0	275.0
1949	1933.5	407.5
1950	2143.5	624.5
1951	1966.5	721.5
1952	2017.5	889.0
1953	2041.0	1067.0
1954	2037.5	1179.0

^a Figures based on AASGP data, taking into account industry coverage.

Without syndets the rate of growth of phosphorus production has not been so spectacular. A new use has been the conversion of phosphorus to pure phosphoric acid for application in liquid fertilizers (7). This probably accounts for some of the increase from 1952 to 1953. Thus far liquid fertilizers made from pure phosphoric acid, ammonia, and other nitrogen-containing materials, and in some cases potassium chloride, have had the greatest development in California, with some use in Texas and the Middle West. While these fertilizers appear to be meeting with acceptance, it is too early to judge their future potential quantitatively. The use of dicalcium phosphate in animal feeds has become increasingly important in the last few years but the market represented by this product is shared between pure acid made from phosphorus and crude phosphoric acid made by treating phosphate rock with sulfuric acid. One producer of by-product ammonia converted his plant to manufacture diammonium phosphate, using pure phosphoric acid made from phosphorus, instead of ammonium sulfate in 1954 (5). If others follow suit, the demand for phosphorus could be significantly increased.

The many compounds, both inorganic and organic, into which phosphorus finds its way will undoubtedly continue to increase in consumption but there does not appear to be any major new use which will compare with the syndets in the foreseeable future. Barring the emergence of some such major new use, it seems probable that phosphorus used in products other than syndets will be of the order of 140,000 tons by 1960, an increase of some 40,000 tons above 1954. Added to the projected increase in phosphorus used in syndets, this suggests new requirements of some 65,000 tons by 1960, or a total of the order of 332,000 tons.

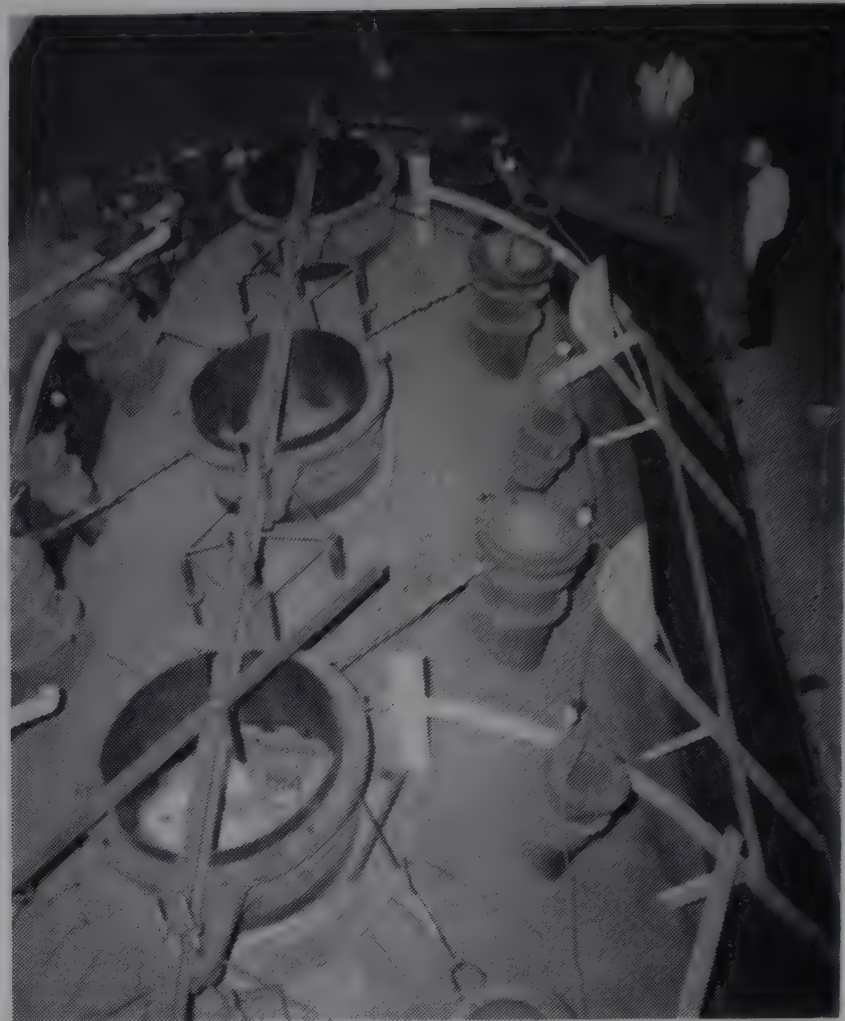
Considering the expansions announced and noted in table of elemental phosphorus producers, construction of new furnaces in the next five years appears to be limited, unless a new major use for phosphorus develops.



Removal of unreacted burden and residual slag begins immediately through electrode holes, and the roof is taken off if replacement is indicated. Jack hammers are used to break up the charge that has solidified, and occasional small charges of dynamite are used to expedite the job.

Normally, all charge and slag is removed down to the carbon hearth. The hearth is cleaned and erosion measured and recorded as a guide for future furnace design and establishment of kilowatt load, voltage-amperage ratio, burden composition, and other operational standards. The carbon lining is then removed as required.

The furnace is then rebuilt. Carbon blocks for the crucible are cemented in place, and several course of fire brick are laid at the top of the crucible. An expandable steel form which fits



furnaces No. 1, 2, and 3 has been developed to reduce time and cost for repouring the arch.

When the electrode becomes too short for further holder slipping, a new electrode section is added. A graphite nipple is screwed into the upper end of the old electrode, the next electrode section screwed onto the protruding nipple, and the holder slipped past the joint.

For safety reasons, power input is interrupted during the electrode building operation. During such delays, maintenance men inspect and make minor repairs to the furnace and auxiliaries, such as electrode seal ring replacement, tapping monkey replacement, etc. Shrouds and cooler castings are replaced each 6 months.

Effective operation and recovery of phosphorus from shale is primarily a chemical reaction that takes place only at elevated temperatures. The chemical reaction proceeds properly only if the materials are present in stoichiometric quantities and in the proper physical form. The process department specifies sampling procedures and provides necessary analytical services for process control. Chemical and screen analyses are made on routine samples of raw materials, intermediate products, and final products to provide a factual basis for establishing raw material specifications and operating standards. Adequate analytical precision is maintained in the laboratory by the frequent analysis of standard samples. Outside-of-standard operations are promptly called to the attention of the production department so corrective measures can be taken.

An important phase of process control is periodic evaluation of operating and control data to identify any significant trends affecting process efficiencies and costs. When necessary, special tests are conducted on production equipment to determine reasons for poor performance.

Most of the development directed toward improvement or modernization of the process is carried out by the process department. The research department is available for carrying out portions of the work requiring specialized equipment or personnel. Any desirable changes in operating procedures indicated by operating and control data are tried in production equipment

if the risk of jeopardizing production is not too great. Otherwise, changes are investigated on bench and pilot scales before adoption in the plant. Before any new equipment or processes are adopted in the plant, they are studied on a pilot plant scale to determine operational and economic feasibility. Initial operations of new equipment or processes on a production scale are carried out under the supervision of the process department. The purpose of initial operation is to establish optimum operating conditions and to train operating personnel.

Since the plant uses three distinct raw materials, none of which is constant in analysis from batch to batch, extensive sampling and analytical programs are constantly under way to assure proper physical and chemical balance of the operation.

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- (2) *Chem. & Eng. News* **32**, 3873, 1954.
- (3) Chemical & Rubber Industry Report, Vol. 1, No. 2, December 1954.
- (4) *Ibid.*, Vol. 2, No. 3, March 1955.
- (5) *Chemical Week*, Feb. 5, 1955.
- (6) Chemicals & Drugs Industry Report, November 1949.
- (7) *J. Ag. Food Chem.* **3**, No. 11, 909, (1955).
- (8) Ruhlman, E. R., "Phosphate Rock," a chapter in Bulletin 556, Bureau of Mines, Department of Interior, U. S. Government Printing Office, Washington 25, D. C., preprint, 1955.
- (9) Tennessee Valley Authority, "Phosphorus—Properties of the Element and Some of Its Compounds," Chemical Engineering Report No. 8, U. S. Government Printing Office, Washington 25, D. C., 1950.
- (10) *Ibid.*, "Production of Elemental Phosphorus by the Electric Furnace Method," Chemical Engineering Report No. 3, Tennessee Valley Authority, Knoxville, Tenn., 1952.
- (11) Waggaman, W. H., "Phosphoric Acid, Phosphates, and Phosphatic Fertilizers," 2nd ed., Reinhold Publishing Corp., New York, 1952.

Important Analyses

Raw Materials. A 2% cut is taken from the shale car loading belt at the mine. Specifications call for the ore to average 24% phosphorus pentoxide, with a 22% minimum. Cars are not unloaded until the analytical laboratory passes the material. A coke sample is taken from each car when unloaded. These samples are combined weekly by source from which purchased and analyzed for fixed carbon, moisture, and size distribution. Results are used for price determination and for guidance in future coke purchases. Moist and dried coke are analyzed each shift for moisture control. Silica is sampled as received from the quarry and again in the proportioning bin. It is analyzed regularly for silica and periodically for alumina, iron, and lime.

In Process. Samples are taken every shift from the pug mill feed and analyzed daily for phosphorus pentoxide, silicon dioxide, ignition loss, and moisture; muller product is sampled and analyzed each shift for moisture. Dried pellets are sampled each shift and analyzed for moisture (4% maximum) and size (mean size of 0.60 inch, with at least 80% plus 1/4 inch). All analyses at pug mills, mullers, and dryers are compared with established standards and used by the operating department for guidance and control of the operation.

Kiln feed is analyzed each shift for moisture and daily for phosphorus pentoxide, silicon dioxide, and calcium oxide. Kiln product is screen analyzed each shift to determine product size and amount of fines produced, and kiln stacks are analyzed for dust loading and effluent emission. Each bin in the proportioning building is

sampled as filled and analyses are converted to feed settings on the weigh feeders for proper proportioning of furnace feed. Weigh feeders are calibrated daily by batch weighings.

Products and By-products. Slag samples are taken during each tap and analyzed each shift for phosphorus, calcium, silicon, aluminum, and iron. These results are used to adjust furnace burden and determine losses. If phosphorus pentoxide rises above the tolerance for instance, potential production is being lost in the slag, and additional coke is added to the burden. If lime to silica weight ratio falls outside the 0.80 to 0.90 standard, adjustments may be made in silica in the burden.

Samples are taken during each ferrophosphorus tap and analyzed weekly for phosphorus, iron, vanadium, chromium, and silicon to determine production.

Precipitator dust is analyzed for phosphorus pentoxide and potassium oxide by standard methods of Association of Official Agricultural Chemists for fertilizers and trace elements.

Water in phosphorus sumps is checked each shift for acidity, with soda ash being added to the sump to neutralize acid as needed. Acidity of tank cars is checked by car loading personnel. If material is not at a pH of at least 8, soda ash is added to each car to inhibit corrosion.

Gaseous effluents and plant waste water are under continuous surveillance by the process department as a part of the industry-agriculture good neighbor program.

Processing equipment

- (1E) Adams Co., Inc., R. P., Buffalo 17, N. Y., porous tube filter, Model CVF-5S.
- (2E) Agitair, Inc., New York, N. Y., furnace, Size 9, Type R.
- (3E) Buffalo Forge Co., Buffalo 4, N. Y., positive displacement fan, No. 13, Type SSL.
- (4E) Food Machinery & Chemical Corp., Pearless Pump Div., San Jose, Calif., four-stage centrifugal pump, Model 8LA.
- (5E) Fuller Co., Catasauqua, Pa., air-quenching, inclined rate cooler.
- (6E) General Refractories Co., Philadelphia 2, Pa., Hiac or Superac standard fire brick.
- (7E) Gruendler Crusher & Pulverizer Co., St. Louis 6, Mo., double roll crusher.
- (8E) Hardinge Co., Inc., York, Pa., Feedometer constant volume feeder, Size C.
- (9E) Hewitt-Robins, Inc., Stamford, Conn., car shaker.
- (10E) Holmes & Bros., Inc., Robert, Danville, Ill., Baughman Verti-Vane thermal coal dryer, Model 7.
- (11E) Jeffery Manufacturing Co., Columbus 16, Ohio, Flextooth crusher, Series 6996, Type F.
- (12E) *Ibid.*, roll crusher, Model 24 X 30.
- (13E) Link Belt Co., Chicago 1, Ill., belt feeder.
- (14E) Merrick Scale Manufacturing Co., Passaic, N. J., Feedoweight weigh feeders, Model WS.
- (15E) Minneapolis-Honeywell Regulator Co., Philadelphia 44, Pa., Brown ElectroniK strip chart recorder.
- (16E) Minneapolis-Honeywell Regulator Co., Minneapolis 8, Minn., Tel-O-Set controller, Type 33-R-24-AN-4.
- (17E) Nash Engineering Co., The, South Norwalk, Conn., compressors, Model K-7 on furnaces No. 1, 2, and 3; K-9 on No. 4.
- (18E) National Carbon Co., New York 17, N. Y., electrodes.
- (19E) Patterson Foundry & Machine Co., The, East Liverpool, Ohio, mullers.
- (20E) *Ibid.*, pug mills.
- (21E) Proctor & Schwartz Inc., Philadelphia 20, Pa., conveyor dryer.
- (22E) Stephens-Adamson Manufacturing Co., Aurora, Ill., live roll grizzly.
- (23E) Traylor Engineering & Manufacturing Co., Allentown, Pa., kilns.
- (24E) Tyler Co., The W. S., Cleveland 14, Ohio, mechanical screen, Type F-600.
- (25E) *Ibid.*, Hum-Mer screen, Type 38.
- (26E) *Ibid.*, Niagara screen, Type 300.
- (27E) Western Precipitation Corp., Los Angeles 15, Calif., Cottrell precipitators, Type A.
- (28E) *Ibid.*, Multiclone cyclone separator, Model P-21396-A, Type 9VG-12.
- (29E) *Ibid.*, Multiclone separator, Model P-39577A, Type 9-VG.
- (30E) Westinghouse Electric Corp., Pittsburgh 30, Pa., Rototrol electrode control, Type RF.

Note: This article appeared in Industrial and Engineering Chemistry in January, 1956

Natural Gas Hydrocarbons for Petrochemicals



ALBERT S. HESTER, Associate Editor

in collaboration with

JAMES F. McDONALD

National Petro-Chemicals Corp., Tuscola, Ill.

EXTRACTION plants for removing higher hydrocarbons from natural gas as liquified petroleum gases or natural gasoline have been common in the petroleum industry for many years (1, 5). Of greater interest from the standpoint of raw materials for the chemical industry are those plants which extend extraction beyond propane, the lowest member of the paraffin series usually extracted for fuel, to include ethane as well. Ethane, from either natural gas or petroleum refinery gases, is an important source of ethylene, which, in turn, can be converted into a host of petrochemicals.

At the Tuscola, Ill., plant of the National Petro-Chemicals Corp., (2, 3, 6-8, 10) ethane is extracted from a natural gas stream and used as the starting material for a series of chemical processes. Higher hydrocarbons, currently sold for chemical or fuel use elsewhere, are extracted at the same time while methane, which makes up the bulk of the gas, is returned to the pipeline stream and continues on to fuel consumers. Ethane is thermally cracked to give ethylene and hydrogen. The latter is com-

bined with nitrogen to make ammonia, part of which is converted into ammonium nitrate. The ethylene is used for synthesis of polyethylene, ethyl chloride, and ethanol. At Tuscola, the unconverted ethylene from the polyethylene unit can be profitably used in the other processes without the necessity of recycling and consequent elaborate repurification. This is only one of the many advantages of a large integrated facility.

National Petro-Chemicals was formed in 1951 by National Distillers Products Corp. and Panhandle Eastern Pipeline Co. Panhandle owns 40% and National Distillers, which operates and manages the company, owns 60%. National Distillers, wishing to diversify its business outside the alcoholic beverage industry, entered the chemical industry in 1947 through a subsidiary formed to manufacture metallic sodium and chlorine at Ashtabula, Ohio. In 1951, U. S. Industrial Chemicals, Inc., was merged into National Distillers. That year the company also purchased a 20% interest in Intermountain Chemical Corp., which mines trona (natural soda ash). The next year National

acquired Algonquin Chemical Co., a manufacturer of caustic soda, chlorine, and sulfuric acid. Desiring an even broader chemical base, National Distillers decided to go into petrochemicals; National Petro-Chemicals Corp. was formed (9), and the Tuscola plant was built.

Several factors contributed to the selection of the Tuscola site. In the first place it is next to a Panhandle Eastern compressor station at the junction of gas lines from separate fields: northwest Texas-Oklahoma-Kansas, and Texas-Louisiana. It is served by three railroads and two major highways. Water is available from the Kaskaskia River. The plant was built on a flat site, which had previously been farmland, four miles west of the town of Tuscola, about midway between the important Chicago and St. Louis marketing centers.

Engineering work began in the early summer of 1951. Two years later, in July 1953, construction was essentially complete and the extraction, fractionation, ethylene, ethyl chloride, and ethanol units, as well as the U. S. Industrial sulfuric acid plant, were operating. Initial investment was approximately \$50 million. Polyethylene and ammonia units were added later; both came into production in 1955. Natural gas reforming units for additional hydrogen for ammonia synthesis were also completed that year.

First extraction plants were for natural gasoline

The first hydrocarbon material extracted commercially from natural gas was casinghead gasoline condensed by piping gas from petroleum wells through cold river water starting in 1903 (1). Later on, plants involving compression and cooling were developed to increase yields; oil-absorption processes were developed still later.

Natural gas companies first set up natural gasoline plants to remove the heavier hydrocarbons which condensed in their pipelines and interfered with transmission. Propane, butane, and some lighter material were also removed along with the gasoline. At first, these hydrocarbons were reinjected into the gas stream, but as markets developed propane and butane became valuable as liquefied petroleum gas (LPG) fuels. As more and more propane and butane were extracted, ethane in equilibrium with the other hydrocarbons became available for extraction. Carbide and Carbon Chemical Co. became interested in high-ethane vent gas streams from gasoline plants as a source of chemical raw materials. When collection from natural gasoline plants eventually became unable to supply the demand, Carbide was forced to build its own ethane extraction plants in West Virginia. These are low-temperature condensation plants which work best on gas streams rich in heavier hydrocarbons.

The first plant to use a relatively ethane-lean gas was one put up by Tennessee Gas Transmission at Gabe, Ky. It, too, is a low-temperature condensation plant. Light hydrocarbons are sent to the Olin-Mathieson plant at Brandenburg, Ky. All fractions but the ethane are sold. Ethane is cracked into ethylene, which is then converted into ethylene oxide, ethylene glycol, ethylene dichloride, polyglycols, and glycol ethers.

The next large, high-extraction unit was the National Petro plant. It uses an oil-absorption process, thought by its designers to be superior to condensation plants when gas relatively lean in higher hydrocarbons must be extracted.

While it does not extract ethane from natural gas, Dow does separate it from LPG at Freeport, Tex.

The Hypersorption process of Union Oil Co. of California is used for extraction of light hydrocarbons from feed streams containing unsaturated hydrocarbons rather than natural gas. However, most pilot plant work on the process was carried out on natural gas, and in 1948 Rohm & Haas installed a Hypersorber in its Houston, Tex., plant for production of high-purity methane from natural gas. But technological improvements

eliminated the need for high-purity methane, and the plant was shut down.

A solid absorbent is used in a fluid bed system in Hypersorber units. The advantage of this process lies in its ability to use lean feedstocks and obtain high component recoveries. When low recoveries can be tolerated, the Hypersorption process may not be economical. When higher recoveries of desired components from natural gas become more economically pressing, the Hypersorption process will probably acquire a greater demand.

Process is fundamentally simple, but refinements are needed to ensure efficient separation

The extraction process at Tuscola consists of only two main steps: absorption from the gas of hydrocarbons above methane in the paraffin series in a light oil; and distillation to separate the oil and hydrocarbons. Separation of hydrocarbons is not exact, so a number of other operations must be added to the two basic ones to achieve efficiency. Figure 1 shows the flow sheet for the extraction and fractionation units.

Fractionation and Adsorption Column Data (26E)

No.	Name	Height	Number of Trays	Tray Type
(1C)	Light oil absorbers (2)	87'	28	Kaskade (22E)
(2C)	Demethanizer	55'	16	Kaskade (22E)
(3C)	Light oil stills (2)	128' (total)	12 (stripping section) 19 (rectifying section)	Kaskade (22E) Kaskade (22E)
(4C)	Reabsorber	73'	28	Bubble cap
(5C)	Pre-absorber	32'	10	Bubble cap
(6C)	Heavy oil absorbers (3)	57'	19	Bubble cap
(7C)	Heavy oil still	64' (total)	13 (stripping section) 10 (rectifying section)	Bubble cap Bubble cap
(8C)	De-ethanizer	73'6"	26	Bubble cap
(9C)	Depropanizer	89'6"	40	Bubble cap
(10C)	Debutanizer	87'6"	40	Bubble cap
(11C)	Deisobutanizer	77' (1st section) 79' (2nd section)	35 35	Bubble cap Bubble cap

As the gas is stripped of its higher hydrocarbons in the light oil absorption towers it picks up a certain amount of the oil. To recover it, stripped gas is sent through a second set of absorption towers, the heavy oil absorbers. The heavy oil from the towers is sent to the heavy oil still for recovery of light oil, which is then returned to process.

Along with the higher hydrocarbons, the light oil in the absorbers takes up a small quantity of methane which is removed in the demethanizer before the light oil distillation.

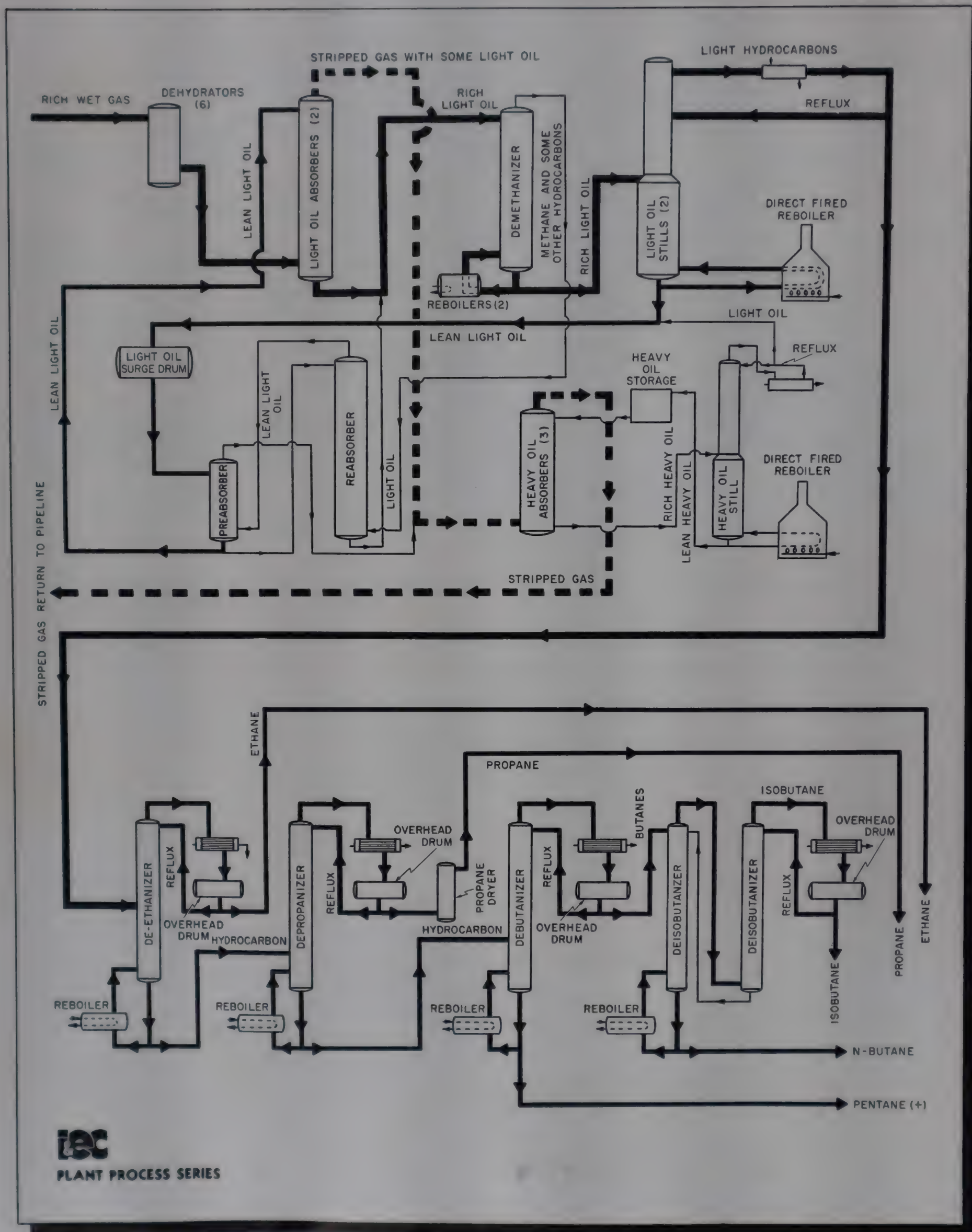


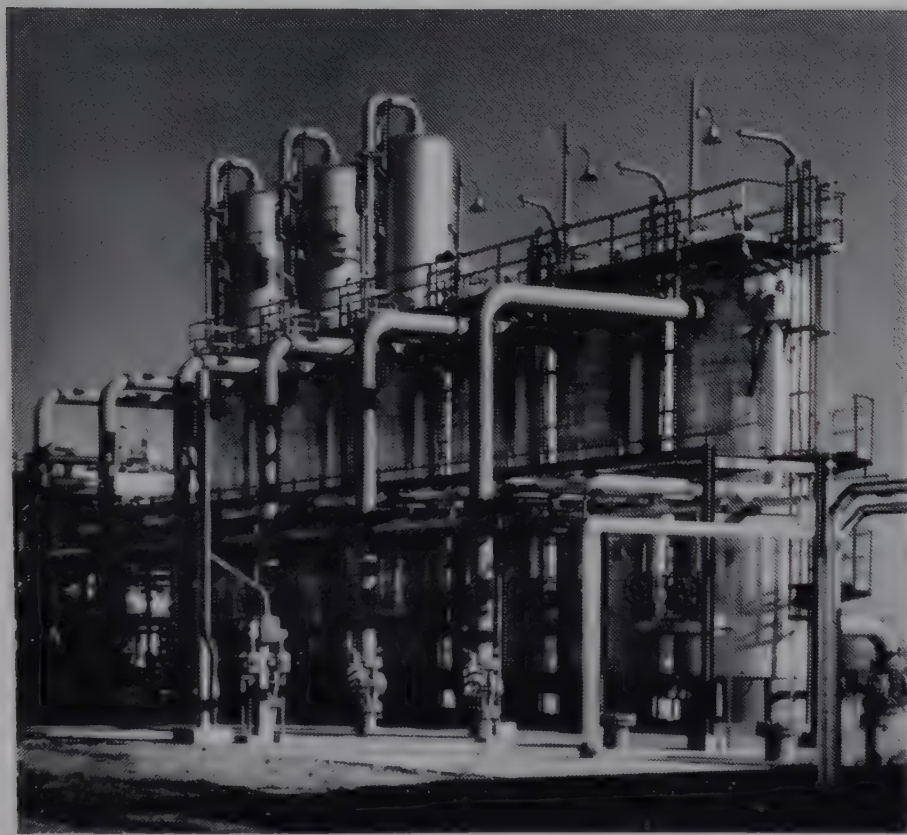
Figure 1. Flow sheet of natural gas hydrocarbons for petrochemicals at National Petro-Chemicals Corp., Tuscola, Ill.

Methane from the demethanizer carries some other hydrocarbons with it, and these are absorbed in light oil in two special columns. In the first, the reabsorber, the light oil absorbs enough hydrocarbons to warrant sending it to the rich light oil stream leaving the main light oil absorbers. The second column, the preabsorber, picks up most of the remaining small quantity of higher hydrocarbons. The main light oil stream is utilized as an absorption medium in the preabsorber before it enters the light oil absorbers.

Hydrocarbons from the light oil still are sent to the fractionation plant. Here four fractionating columns (one of them in two sections) separate the stream into ethane, propane, normal butane, isobutane, and natural gasoline.

Gas must be dried before processing

Gas from the Panhandle Eastern Pipeline pumping station enters the National Petro-Chemicals plant through the metering station, where it is possible to keep accurate records for cost purposes of gas entering and leaving the plant. The plant is designed to process 400 million standard cubic feet of gas per day at 500 pounds per square inch gage pressure and 60° F. Design was on the basis of a maximum pressure of 625, and a minimum of 425 pounds per square inch, with a maximum flow rate of 425 cubic feet.



Six dehydration towers (26E) remove moisture from the gas stream. Gas enters the top of each tower through a 16-inch motor-operated valve and leaves through a similar valve at the bottom. Moisture is absorbed by three layers of dessicant contained by screens. Top and bottom layers consist of bauxite (21E) three feet thick. Between them is a 9½-foot bed of a siliceous absorbent (25E). Designers thought that packing of the dessicant might eventually increase pressure drop and reduce the flow rate, but this problem has not arisen during operation.

To prevent freezing and hydrate formation during absorption, gas is dehydrated first. Design called for removal of 7 pounds of water per million standard cubic feet, but, in practice, about 15 pounds has been more usual. In normal operation four towers connected in parallel are in use for dehydration, while one is being regenerated and one cooled.

Ethane and higher hydrocarbons are absorbed in light oil

Hexane was selected as the light oil for absorbing hydrocarbons from the gas stream. Refrigerated light oil passes through the preabsorbers, where the low temperature is maintained. Refrigerated dry gas flows upward against the light oil stream. Rich light oil containing ethane and higher hydrocarbons plus a



The two absorption columns (1C) are connected in parallel. Dried gas is cooled to -20° F. (3H) and then flows upward through the column. Light oil, also cooled to -20° F., (4H) flows downward. The light oil comes to the absorbers from the light oil surge drum, a 10-foot-diameter, horizontal, pressure vessel 30 feet long. Light oil circulation pumps (3E) bring the oil from the drum to the preabsorber and the light oil booster pumps (3E), followed by the light oil auxiliary booster pumps (14E), take the oil to the absorbers. A pressure of 720 pounds per square inch gage is developed. Two propane-cooled intercoolers (5H) maintain the -20° F. temperature in each tower. Flow of rich light oil from the bottom of the absorbers is governed by a liquid-level controller. Combined streams from the two absorbers are warmed to 70° F. (4H) before going to the demethanizer.

The rich light oil, with the desired hydrocarbons, also contains some methane. This is removed in the demethanizer (2C). Rich oil is fed in at the top, and two kettle-type reboilers (6H) at the bottom supply heat for methane removal.

The reboilers are heated by a stream of lean light oil (7H). Additional heat is furnished by external heating of material on the 10th tray. The methane leaving the demethanizer as overhead goes to a reabsorber for marginal recovery of ethane and propane prior to return to the pipeline. Rich light oil from the bottom of the demethanizer is sent to the light oil stills, after it is preheated to 410° F.

Extracted hydrocarbons are separated from light oil in two light oil stills (3C). Each consists of a rectifying and stripping section. Two pumps (15E) circulate the lean light oil bottom product through each still's gas-fired reboiler furnace (1E) which keeps temperature up to 410° F. Intermediate reboilers heat liquid from the 6th tray of the stripping section (7H).

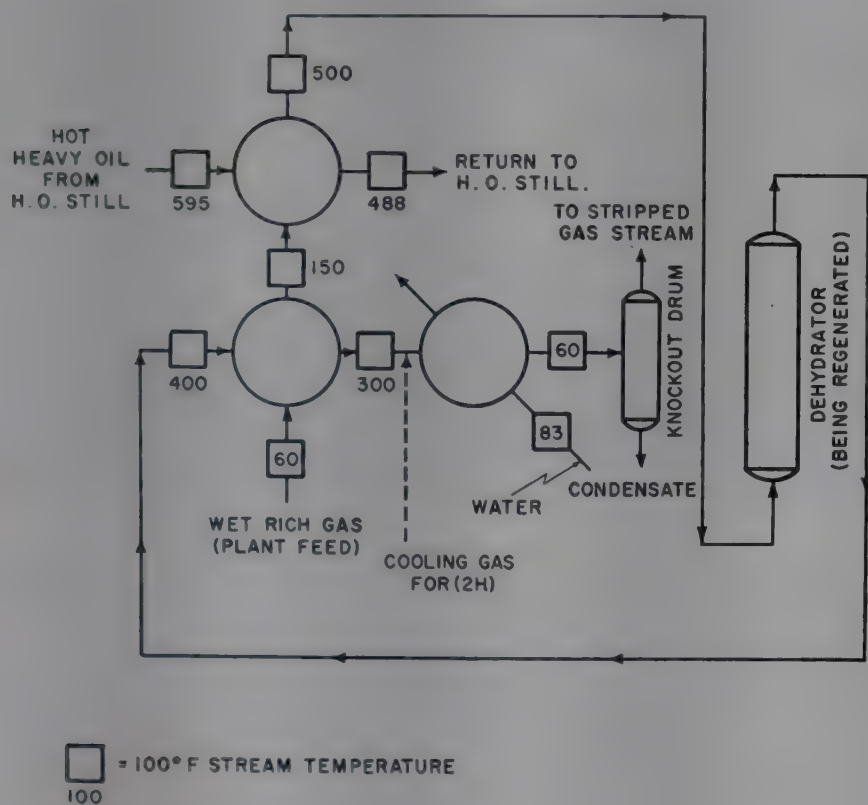
small amount of methane is warmed, fed to the demethanizer, and then to the light oil stills, where the desired hydrocarbon products are removed from the absorbent.

HEAT EXCHANGE DATA

(1H) Feed gas is heated in two exchangers for regenerating dehydrators, and then cooled before returning to the stripped gas stream.

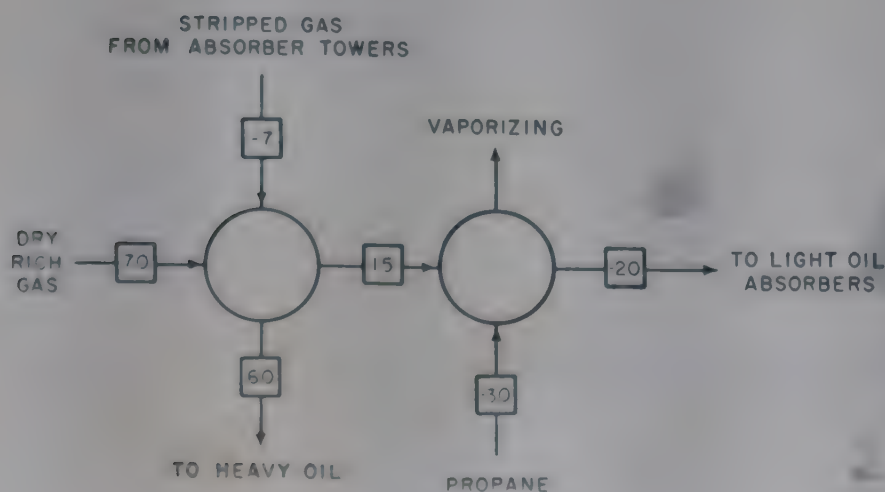
A stream of wet inlet gas, heated to 500° F. (1H), flowing upward through the tower regenerates the dessicant. During this process dessicant temperature reaches 330° to 400° F., leveling off at the latter point when all water has been removed. Three hours are allowed for this. Regenerating gas is cooled to 60° F. when it leaves the dehydrator and is then sent through the re-activation knockout drums. These are vertical tanks, 48 inches in diameter and 12 feet tall. Gas enters and leaves near the top and condensate settles in the bottom. A liquid-level controller allows condensate to flow out through measuring tanks. The gas is then returned to the stripped-gas stream leaving the plant.

A duplicate system, consisting of a knockout drum and three exchangers, is included for use with the dehydration tower undergoing cooling. Wet rich gas from the inlet stream cools the bed by flowing downward through the tower for 3 hours. Gas leaving the tower is cooled to 60° F. (2H), flows into the knockout drum, and then joins the gas stream from the other knockout drum before returning to the stripped-gas header.

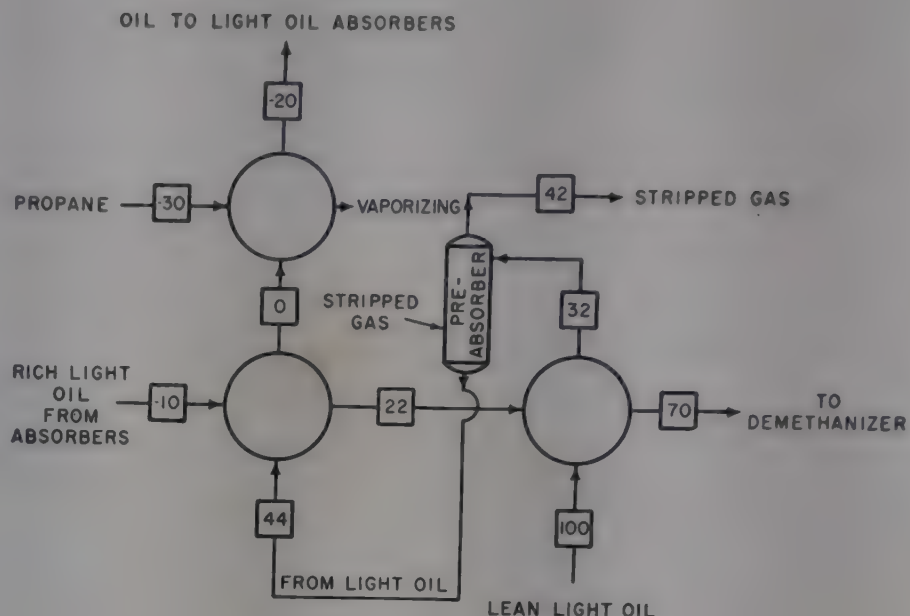


(2H) Cooling of gas used to cool dehydrators immediately after regeneration is carried out in equipment duplicating (1H), but only the water-cooled exchanger is used. Equipment for (1H) and (2H) is interchangeable.

(3H) Dry gas is cooled to -20° F. before going to light oil absorbers.



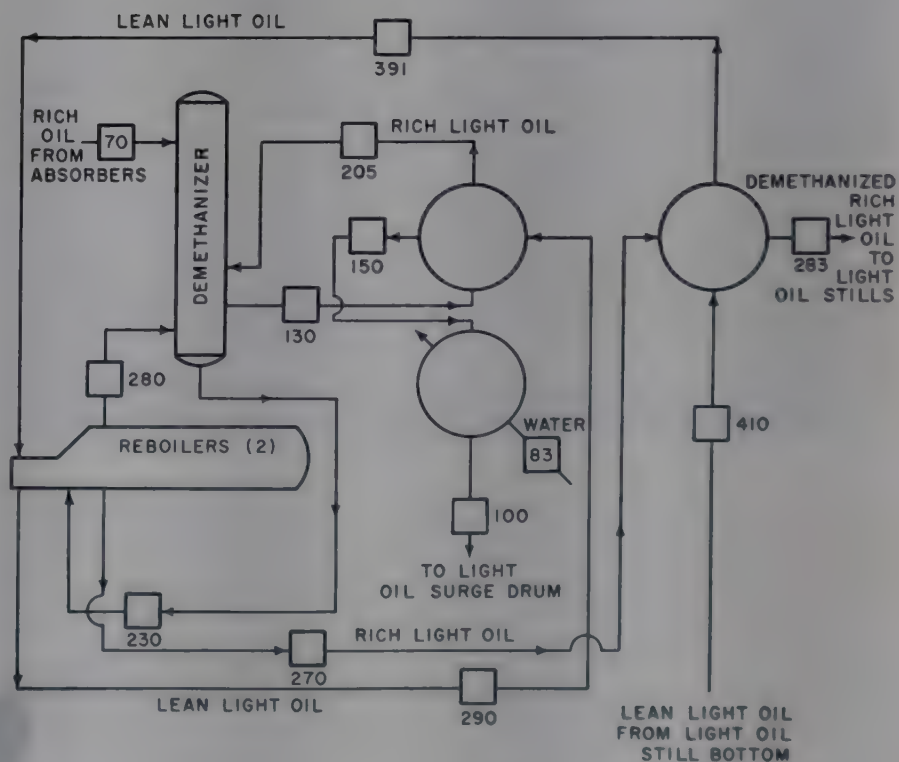
(4H) Light oil must be cooled to -20° F. before going to light oil absorbers.



(5H) Intercoolers maintain low temperature in light oil absorbers.

Each tower has two vaporizing propane (-30° F.) exchangers. The first cools -5° F. oil from the 6th tray to -20° F. and returns it to the 7th tray. The second cools -2° F. oil from the 24th tray and returns it to the 25th.

(6H) Demethanizer reboilers are heated by lean light oil from the light oil still bottoms. Before going to the reboilers the light oil stream is used to preheat the light oil still feed (demethanizer bottom product). After leaving the reboilers the light oil stream is used to maintain temperature of material from the 11th tray of the demethanizer.



(7H) Each of the two light oil stills has a gas-fired reboiler furnace which vaporizes the 410° F. bottom material and returns it to the still. Intermediate reboilers on each still raise the temperature of material from the 34th tray from 365° to 375° F. and partially vaporize it. Heavy oil, 595° F., from the bottom of the heavy oil still is used to heat the intermediate reboilers. It is cooled to 495° F. in the process.

Light oil still feed (from the demethanizer reboiler) is preheated from 270° F. to 283° F. in an exchanger (one for each still) by the light oil still bottom product. Bottom product is cooled from 410° to 391° F.

- (8H) Overhead vapors at 140° F. from each light oil still are partially condensed in a reflux condenser and cooled to 100° F. Cold (89° F.) water is the coolant.
- (9H) Hydrocarbon product from the light oil stills (via reflux drum) is completely condensed and cooled from 100° to 75° F. in the -48° F. propane-cooled overhead condenser.
- (10H) Demethanizer overhead gas is cooled from 75° to 46° F. Coolant is -7° F. reabsorber overhead gas, which is warmed to 65° F. before going to the preabsorber.
- (11H) Reabsorber intercooler cools 6th tray liquid from 0° to -20° F. and returns it to 7th tray. Propane, at -50° F., is the coolant.
- (12H) Second reabsorber intercooler is similar to (11H) and liquid from 24th tray is cooled and returned to the 25th.
- (13H) Lean heavy oil is cooled from 90° to 50° F. in a propane-cooled exchanger before going to the heavy oil absorbers.
- (14H) Lean heavy oil from (15H) is cooled from 234° to 90° F. by exchange with 61° F. rich heavy oil from the heavy oil absorbers. The rich heavy oil is heated to 200° F.
- (15H) Lean heavy oil from the bottom of the heavy oil still (595° F.) is used to preheat rich heavy oil from (14H) from 200° to 540° F. before it is fed into the still. The lean heavy oil then goes to (14H).

(16H) A water-cooled exchanger condenses overhead from the heavy oil still. The 240° F. vapors are cooled to a predominantly liquid product at 100° F.

(17H) Product from the extraction unit (LPG) is warmed from 80° to 125° F. with 65 pound per square inch gage steam in the de-ethanizer preheater.

De-ethanizer reboiler is heated by 65 pound per square inch gage steam. Liquid, 190° F., is heated to form 200° F. vapor.

De-ethanizer overhead condenser is propane-cooled. Normally 63.5° F. vapor is partially condensed to a 58° F. vapor-liquid mixture.

(18H) Hydrocarbons from the de-ethanizer reboiler (at 117° F.) are fed to the depropanizer. Depropanizer reboiler is heated by 65 pound per square inch gage steam. Liquid, 200° F., is heated to 205° F. vapor. Overhead condenser is water-cooled. Vapor at 112° F. is condensed to 105° F. liquid.

(19H) Butanes and pentanes from the depropanizer reboiler (161° F.) are fed to the debutanizer. Debutanizer reboiler vaporizes 217° F. liquid to 230° F. vapor. Overhead condenser converts 160° vapor to 150° F. liquid.

(20H) Butanes (debutanizer overhead, 150° F.) are fed into the deisobutanizer. Reboiler converts 145° F. liquid to 150° F. vapor. Overhead condenser condenses 118° F. vapor to 116° F. liquid (150-isobutane). Bottom product (*n*-butane) is cooled from 150° F. to 100° F. in an exchanger.

A liquid-level controller at the bottom of each absorber tower controls flow of rich heavy oil to the heavy oil still (7C). The stream leaving the absorber tower is heated to 200° F. (14H) before it enters the flash drum, a vertical tank 48 inches in diameter and 8 feet tall. Gas from the top of the drum is combined with the recycle gas separated from the overhead stream leaving the still by the overhead drum. Liquid product from the bottom of the flash drum goes to the heavy oil still. Feed for the heavy oil still is heated from 200° to 540° F. (15H) before entering the column. A gas-fired furnace is used as a reboiler (2E). The hot heavy oil from the bottom of the still is used for heat exchange several places in the plant (1H, 7H). When cooled to 90° F., it is returned to the heavy oil storage tank.

The light hydrocarbon vapors at the top of the still are cooled to 100° F. (16H) before going to an overhead drum, a horizontal tank 6 feet in diameter and 18 feet long. Vapor from the drum (recycle gas) is compressed (29E), sent through a knockout drum, and used for fuel in other parts of the plant. The condensed material not pumped (17E) from the drum back to the top of the tower for reflux is sent back to the light oil surge drum.

Overhead from the light oil stills, at a temperature of 140° F., passes through reflux condensers (8H) and then to a reflux drum in a combined stream. The drum is a vertical tank 5 feet in diameter and 15 feet tall. Reflux is returned to the top of the stills by the two reflux pumps (4E). Liquefied and gaseous material from the partially condensed overhead is cooled in a propane exchanger (9H) and sent to the light oil overhead drum.

Liquid hydrocarbon product is then sent by two pumps (5E) to the fractionation unit.

The demethanizer removes not only methane from the light oil, but also small quantities of ethane and propane, which are recovered. Overhead from the demethanizer is cooled to -20° F. (10H) and then sent up through the reabsorber (4C) where it comes in contact with cold light oil. Two propane intercoolers, one between 6th and 7th tray (11H), the other between 24th and 25th tray (12H), keep the light oil cool. Oil from the bottom of the reabsorber is pumped (16E) back into the rich oil stream leaving the light oil absorbers.

Overhead from the reabsorber is then sent to the preabsorber (5C) to remove almost all of the ethane.

Absorption is by the main stream of light oil, which flows through the preabsorber before going to the light oil absorber. Overhead from the preabsorber goes to a vertical knockout drum 42 inches in diameter and 8 feet tall. It then goes to the preabsorber overhead compressors (28E) which raise the pressure enough to return the stripped gas to the pipeline stream.

Stripped gas from the top of the light oil absorbers contains a considerable amount of light oil, which if not recovered, would amount to a loss of over \$2 million per year. Heavy oil of molecular weight 180 is used in the three heavy oil absorbers (6C) which recover light oil. A storage tank 25 feet in diameter and 18 feet high serves as a reservoir for the heavy oil. From the storage tank the oil is pumped (6E) through the propane-cooled heavy oil chiller (13H) and to the 4th tray of the heavy oil absorbers. Overhead from the absorbers is returned to Panhandle Eastern.



Exhaust steam at 65 pounds per square inch gage, supplies reboiler heat for these columns. The LPG stream is heated in a preheater (17H) before entering the de-ethanizer (8C) at the 10th tray.

Overhead is cooled in a propane-cooled condenser and goes to the ethane flash drum, a horizontal tank 90 inches in diameter and 61 feet long. A pump (7E) returns reflux to the top of the column. Other pumps (8E) are available for reinjection of ethane into the natural gas stream if it is necessary in order to maintain B.t.u. content of gas returned to Panhandle Eastern.

Bottom product from the reboiler enters the depropanizer (9C, 18H) above the 18th tray. This column is similar in construction and operation to de-ethanizer and also is provided with reinjection (9E) and reflux (10E) pumps. Cold water is used for the overhead condenser, however, and the overhead drum is somewhat smaller—20 feet long and 72 inches in diameter. Two adsorbers are provided for dehydrating propane before it is sent to storage. One is kept on stream for 8 hours while the other

is being regenerated and cooled. Adsorption towers contain a bed of 4- to 8-mesh bauxite (25E).

Bottom product from the depropanizer goes to the debutanizer (10C) which separates normal and isobutanes from pentanes and heavier components. Feed enters at the 18th tray. Operation and auxiliary equipment (19H) are similar to that of the depropanizer. Bottom product is cooled from 230° F. to 100° F. by a cold water exchanger and then sent to storage, while overhead from the debutanizer is condensed with cold water. Liquid not pumped (12E) back as reflux is fed through an overhead drum to the top tray of the first section of the deisobutanizer (11C, 20H). Intermediate pumps (11E) transfer material from the bottom of the second section to the top of the first. Only the first section is connected to the reboiler. Bottom product is normal butane, which is cooled and sent to storage, as is the isobutane condensed from the overhead. One reinjection pump (13E) serves both butane columns.

Fractionation plant separates hydrocarbons

Liquefied petroleum gas from the extraction plant is separated into its individual hydrocarbon components in the fractionation plant, situated east of the extraction unit. Pressure of the LPG stream is 486 pounds per square inch gage; temperature is 80° F. Fractionation takes place in four columns, the de-ethanizer, the depropanizer, the debutanizer, and the deisobutanizer. Because of the large number of trays required, the deisobutanizer is divided into two separate towers. Ethane is recovered as a gas but all other products are liquid.

If necessary, hydrocarbons may be reinjected into the natural gas stream to maintain B.t.u. content of gas returned to Panhandle

Eastern. In reinjecting hydrocarbons, it is generally more economical to inject the higher hydrocarbons first, and, if the need arises, to add lower hydrocarbons in descending order. Butanes are commonly reinjected, propane less often, and ethane almost never.

The designed product recoveries for the extraction and fractionation plant are 10,050,000 standard cubic feet per day of ethane, 380,000 gallons per day of propane, 21,300 gallons per day of isobutane, 57,400 gallons per day of normal butane, and 18,520 gallons per day of pentanes and higher hydrocarbons (natural gasoline).

In designing the plant, provision was made to treat products

to remove sulfur if any appeared in the gas feed. A caustic treatment unit can remove sulfur compounds from propane before it is sent to the dehydrator, and a sweetener (23E) to convert mercaptan sulfur to less odorous disulfide compounds can be placed in the process stream between the depropanizer and the debutanizer. So far, sulfur content of the gas has never reached any measurable quantity and it has not been necessary to use either of these units.

Refrigeration, cooling water, steam, and instrument air are needed services

Separate units for vaporization of liquid propane and compression and recondensation of high pressure vapor supply the refrigeration needed in the extraction and the fractionation plants.

A seven-cell, forced draft, cooling tower (24E) is used for the cooling water, which must be recirculated. It serves both the fractionation and extraction plants and can cool 30,000 gallons of water per minute from 102° to 83° F.

High pressure steam at 625 pounds per square gage, and also some low pressure steam at 65 pounds per square inch gage are supplied by the power house. The power house is operated on either coal or natural gas.



The refrigeration system in the extraction unit utilizes two steam turbine-driven (27E) centrifugal compressors (18E). High pressure steam enters the turbine at 725° F. and 625 pounds per square inch gage; exhaust is kept at a 26-inch vacuum by means of a surface condenser. Condensate is returned to the power plant.

The fractionation refrigeration unit consists of 2000-horsepower, propane compressors (19E).

Instrumentation reduces personnel requirements

Heavy instrumentation of the plant has resulted in a minimum of operating personnel. Each shift crew consists of four opera-

tors for the extraction unit, three for the fractionation unit, and one truck loader. There are also five process mechanics and three tank car loaders under the supervision of the shift supervisor of the crew working on the daylight shift. Except for them, the area superintendent and his assistant are the only day personnel.



Liquid products are moved from plant via 40 car-loading spots or five truck-loading spots. Extensive storage capacity has been provided for all products except ethane, which is ordinarily moved directly to the ethylene plant. A 1-hour supply is held in the surge tank in the fractionation plant.

Propane presents the biggest storage problem. Two million gallons can be stored in a series of horizontal tanks, which hold the liquid at 200 pounds per square inch gage. Another 6,300,000 gallons can be kept in the underground storage unit, consisting of a shaft 12 feet in diameter, sunk 330 feet into limestone, with a 400-foot horizontal tunnel leading to five parallel, 450-foot, horizontal shafts at the bottom. The big difficulty encountered in underground storage has been leakage around the bulkhead at the bottom of the shaft. This problem has been solved by filling the shaft with water to the depth necessary to counterbalance pressure of the stored gas.

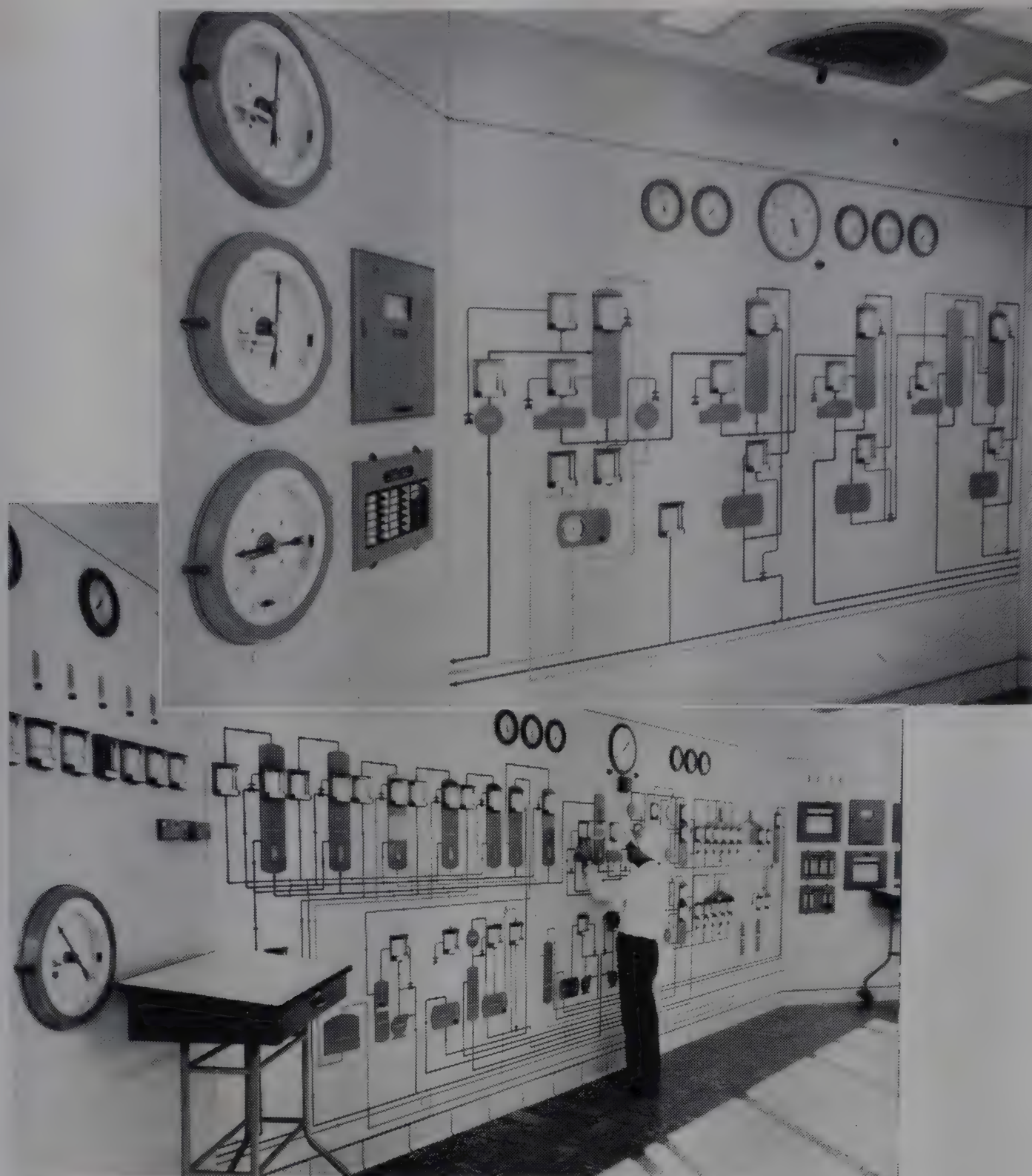
A group of spherical tanks can store 252,000 gallons of isobutane, kept at a pressure of 75 pounds per square inch gage. Similar tanks are used for the 504,000 gallons of normal butane storage capacity. Spherical, as well as horizontal, tanks can hold a total of 145,000 gallons of natural gasoline.

Extensive laboratory control is not needed for this process. Every 24 hours laboratory fractionations are carried out to determine composition of reabsorber tops, light oil absorber overhead, light oil still tops, preabsorber bottoms, and demethanizer bottoms. Feed gas is analyzed occasionally. Nonroutine tests are often made for studies to improve plant performance.

LPG products sold are subjected to a number of laboratory tests: vapor pressure, total sulfur, copper strip corrosion tests, dryness tests, mercury freeze tests, weathering tests, and others.

Continuous expansion is the word at Tuscola

At the present time the demand for butanes is not so good as that for liquefied petroleum gases in general. At Tuscola during the summer most of the normal butane is reinjected into the pipeline. This situation will probably change eventually, however. Isobutane is sold for alkylation processes for producing high octane gasoline.



Extraction and fractionation units have separate instrument panel boards. Flow controllers (5I) are placed on lines bringing feed to the various columns. Valves (2I) determining flow of liquid from the bottom of columns or from reboilers are governed by liquid-level controllers (2I). These instruments all have miniature recording dials mounted on the graphic control panels. Some critical points also have recording temperature indicators

with no control. Others are connected to a multiple-point single-meter temperature-indicating device (4I).

Recording calorimeters (1I) ensure a sufficiently high B.t.u. content for the stripped gas leaving the plant. Furnace operation is checked by an oxygen recorder (3I). Alarms give a warning if liquid levels in the various drums are not within the proper range.

Start-up and shut-down procedures

Before the original start-up, the entire plant was hydrostatically tested by the contractor. After the plant was turned over to National Petro-Chemicals Corp., blanks installed for the hydrostatic test were removed and an air test at 65 per pounds per square inch gage was run. When all leaks were repaired the system was then purged with gas, which was then released to the atmosphere or to the flare system. Dried gas from the dehydration unit was circulated through the system to remove remaining water.

Rapid start-up and Shut-down are possible. In normal start-up operations, which take 5 to 6 hours altogether, the light oil and heavy oil circulation systems are first started. The furnaces, which take 2 to 3 hours to heat up, are next started, and then the refrigeration system is cut on. When these two systems have reached the proper temperatures feed is turned into the plant in several increments.

In a normal shut-down, feed is slowly cut out of the extraction plant and bypassed to the compressor station. Fractionating columns are put on total reflux. Circulation of absorber oils is continued for a short time. Process compressors are shut down when loads on them decrease sufficiently and all residual gases have been sent to the fuel system. Refrigeration is shut down in stages; one compressor is left running until the entire system is cool. Furnaces are cut off immediately, but oil circulation is continued until furnaces are cool. Normal shut-down takes 3 to 4 hours.

In case of power failures, furnaces are shut off first. All circulation of absorber oils stops, but feed gas is allowed to continue to flow through the plant and back to Pan-handle Eastern.

Failure in the instrument air supply has about the same effect as power failure. Steam failures are not usually so troublesome since they are usually merely pressure reductions and not complete stoppages.

Natural gasoline produced at Tuscola is a minor product compared to the other hydrocarbons. It is easily marketed to petroleum refiners.

Expansion of the Tuscola plant makes it desirable to increase ethane output. At present, only about 40% of the ethane from the feed gas is extracted. Plans are being drawn up to modify the extraction plant to increase the amount to about 60%. This will be done by adding more heat exchange equipment so that the feed gas can be cooled more than at present, and also by increasing the oil circulation rate in the absorber.

The Tuscola plant as a whole has been in a state of almost continuous expansion since it was started. Announced plans call for an iso-sebacic acid unit and a phosphoric acid plant. The company also hopes that other companies will take advantage of the chemicals available and participate in the development of an industrial complex around the plant. Several companies have evinced an interest, and already a fertilizer plant utilizing sulfuric acid from U. S. Industrial has been built adjacent to the National Petro-Chemicals plant.

Acknowledgment

The authors are grateful for the background information supplied by E. E. Frye of J. F. Pritchard Co., Kansas City, Mo. They are also indebted to H. F. Johnstone of the University of Illinois for the use of the report of his chemical engineering design class, "A Study of the Design of a Hydrocarbon Recovery Petrochemical Plant," June 1, 1954.

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- (9) Smith, R. A., *Fortune* 48, No. 4, 145-9, 282, 284, 286, 289, 290, October 1953.
- (10) Stark, D. J., *Petroleum Processing* 8, No. 6, 897-9 (June 1953).

Processing equipment

- (1E) Alcorn Combustion Co., Philadelphia, Pa., gas-fired furnace, 493,000 lb./hr., 44 tubes.
- (2E) *Ibid.*, 600,000 lb./hr., 56 tubes.
- (3E) Bingham Pump Co., Portland, Ore., Circulation pump, HSB-H double suction, 1-stage, 3550 r.p.m.
- (4E) *Ibid.*, CF, 1-stage, 1800 r.p.m.
- (5E) *Ibid.*, VTR Vert. can, 6-stage, 3600 r.p.m.
- (6E) *Ibid.*, MSB, 6-stage, 3550 r.p.m.
- (7E) *Ibid.*, VTR, 5-stage, vertical, 1750 r.p.m.
- (8E) *Ibid.*, VTR, 11-stage, 3550 r.p.m.
- (9E) *Ibid.*, HPH-H, high pressure, 10-stage, 3550 r.p.m.
- (10E) *Ibid.*, HCA, 1-stage, 3560 r.p.m.
- (11E) *Ibid.*, HCA, 1-stage, 3540 r.p.m.
- (12E) *Ibid.*, HCA, 1-stage, 3520 r.p.m.
- (13E) *Ibid.*, HPM-H, high pressure, 9-stage, 3560 r.p.m.
- (14E) Byron-Jackson Co., Los Angeles, Calif., booster pump, SM double volute, 3550 r.p.m.
- (15E) *Ibid.*, DSDV, 1-stage, 3550 r.p.m.
- (16E) *Ibid.*, HSM, vertical suction, 1-stage, 3550 r.p.m.
- (17E) *Ibid.*, SM, 2-stage, 3600 r.p.m.
- (18E) Carrier Corp., Syracuse, N. Y., compressors, 6-stage.
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Note: This article appeared in *Industrial and Engineering Chemistry* in February, 1956

The Outlook for LPG's

Many chemical companies are considering extraction operations for high percentage ethane recovery and it seems reasonably sure that a large number of ethane extraction plants will be constructed. Currently being designed is a plant for high ethane recovery for Kentucky Hydrocarbon Co., a subsidiary of the Equitable Gas Co., at Maytown, Ky. It will supply Carbide and Carbon Chemical. Practically every gas transmission company in the United States is currently aware of the value of ethane as a chemical raw material and has considered to what extent extraction operations should be undertaken.

The development of this field at the present time is probably governed as much by the political situation as by anything else. Recent rulings by the Federal Power Commission to the effect that earnings of gas transmission companies could be penalized by undertaking extraction operations, or permitting extraction operations on natural gas flowing through their pipelines, have tended to influence adversely many company managements contemplating extraction operations.

The outlook for ethane depends almost entirely on that for ethylene, to which it is cracked for chemical use. The growing demand for ethanol, ethylene oxide, polyethylene and other ethylene-derived compounds makes it almost certain that ethylene has a very bright future (4). Of course, ethane and ethylene are obtained from petroleum refinery gases as well as from natural gas. Propane and even butane, can also be cracked to produce ethylene.

Propane, butane, and mixtures of the two are finding a steadily increasing market, chiefly for fuel use as LPG. The upward sales trend is expected to continue; the Liquefied Petroleum Gas Association estimates that in 1955 total U. S. sales were 5,850,000,000 gallons, an increase of better than 14% over the previous year. About 50% of total sales usually go to domestic and commercial users and about 20% for chemical and 6 to 8% for synthetic rubber manufacture. Approximately 7% is used as an industrial fuel and 10% for internal combustion engines.

- (21E) Floridin Co., Tallahassee, Fla., Florite.
- (22E) Koch Engineering Co., Wichita, Kan., Kaskade trays.
- (23E) Perco Div., Phillips Petroleum Co., Bartlesville, Okla., sweetener.
- (24E) Pritchard, J. F., & Co., Kansas City, Mo., cooling tower, 7-cell. Two 17-foot-diameter fans each cell, 1800 r.p.m., 40-h.p. motor.
- (25E) Socony-Vacuum Oil Co., New York, N. Y., Sovabead adsorbent.
- (26E) Sun Shipbuilding Co., Marcus Hook, Pa., all absorber, distillation, and fractionating columns; surge drums.
- (27E) Westinghouse Electric Corp., Pittsburgh, Pa., condensing turbines, 4000 hp.
- (28E) Worthington Corp., Harrison, N. J., horizontal compressors, DB duplex, 190-hp. electric motor driven.
- (29E) *Ibid.*, HB horizontal.

Instruments

- (1I) Cutler-Hammer, Inc., Milwaukee, Wis.
- (2I) Fisher Governor Co., Marshalltown, Iowa.
- (3I) Hays Corp., Michigan City, Ind., oxygen recorder.
- (4I) Minneapolis-Honeywell, Philadelphia, Pa., Brown Elektronik multiple-point temperature indicator.
- (5I) Taylor Instrument Co., Rochester, N. Y., Transet recorder (82JF); controllers, BI-ACT (332R) and TRI-ACT (329R).

TANTALUM



CHESTER PLACEK, Assistant Editor

in collaboration with

DONALD F. TAYLOR

Fansteel Metallurgical Corp., North Chicago, Ill.

TANTALUM is best known for its almost complete immunity to corrosion and chemical attack. Although it is not used in such vast quantities as the more common metals, tantalum is essential in a number of varied fields. In fact, it is considered as a material of prime strategic importance.

The major part of today's tantalum production is used in the manufacture of chemical process equipment, and its use for this purpose is rapidly growing (3). Most of the remaining production goes into electrolytic capacitors and electronic tubes, and into surgery. In capacitors alone, tantalum has developed a market estimated at \$5 million a year (2).

Tantalum, atomic number 73, is a member of Group V in the periodic table. A metal with a high melting point, 3000° C. (5432° F.), it is characterized by ease of working and by extremely high resistance to attack by all acids (6) except hydrofluoric acid.

Because the element is always coexistent with niobium in mineral deposits (6, 8), and because the two are chemically similar, some confusion arose at the time of discovery. Hatchett, a British chemist, examined a mineral from Connecticut, and in

1801 described a new acidic oxide of an element. He proposed the name columbium for the element. A year later, Ekeberg of Sweden announced the discovery of another element whose oxide had acidic properties, and he named it tantalum. Wollaston suggested the identity of the two elements. In 1844, Rose showed that certain columbites contained two distinct acids; one a tantalum compound, and the other a compound of a similar element. To the latter he assigned the name niobium. The identity of Hatchett's columbium and Rose's niobium was soon established. The International Union of Chemistry subsequently recommended that the name niobium be assigned to the element to conform with European nomenclature, although usage in American metallurgical industries retains the name columbium.

None of the early investigators succeeded in isolating tantalum until 1903. Small pellets of the metal were then produced in Germany by von Bolton. These pellets were ductile enough to permit working into sheet and wire. Because of its ductility and its high melting point, tantalum wire became the first metallic lamp filament material. Dental and surgical instruments with noncorroding tantalum blades or tips also were produced. World

War I put an end to European attempts at commercial production.

Fansteel Metallurgical Corp., North Chicago, Ill., has been until recently the only American producer of tantalum metal. Kawecki Chemical started commercial tantalum production last March (2).

In 1922, Balke of Fansteel produced ductile tantalum bars (1). The metal found use in battery charging rectifiers, and in "B" power units for radio receivers at that time. During this time, research and development were done for other uses of the metal; notably in the chemical field.

Early production of tantalum and its compounds was sufficient for industrial needs at the time, but in 1940 and 1941 the need became greater. Four months before U. S. entry into World War II, blueprints for a \$5-million tantalum plant were submitted to Washington. In 1942, approval for construction was obtained from the Defense Plant Corp. The plant was quickly built, and was operated under lease by Tantalum Defense Corp., a wholly owned subsidiary of Fansteel. In 1947, Tantalum Defense Corp. purchased the plant under a dormant estate contract, which has since expired.

Tantalum used in corrosive processes

Tantalum equipment has come into extensive use in some of the most severely corrosive processes in the chemical industry. In immunity to corrosion from chemical attack, the element is not surpassed by most other metals or alloys (5, 11). The only acids with which tantalum must be considered with caution are hydrofluoric, fuming sulfuric, hot sulfuric, and hot phosphoric. However, the last two can cause trouble only at high concentrations and pressures. Sulfuric acid (except fuming), when not contaminated with fluoride, can be processed with tantalum equipment at most concentrations and temperatures. Tantalum heaters are used for concentrating sulfuric acid at steam pressures up to 150 pounds (5). With phosphoric acid, tests in the Fansteel laboratory indicate limiting conditions of 175° C. and 85% strength.

Tantalum is also inert to bromine, iodine, and their compounds at temperatures employed in most chemical operations. Neither nitric acid nor aqua regia attacks tantalum at any concentration or temperature at normal pressures.

In practically all chemical plant equipment where tantalum is used, the metal is used as the heat transfer surface. Properly designed and applied tantalum equipment is very efficient. For example, a tantalum bayonet heater, 1.5 inches in diameter and 6 feet long, and having an effective heating area of 2.36 square feet, will evaporate approximately 1 ton of 95% nitric acid per hour at 150 pounds of steam pressure (5). In condensing and cooling operations, similar high efficiencies are obtained.

Owing to the ductility, hardness, and toughness of the metal, considerable quantities of tantalum are currently used in the manufacture of tank and pipe lining, and of tubing.

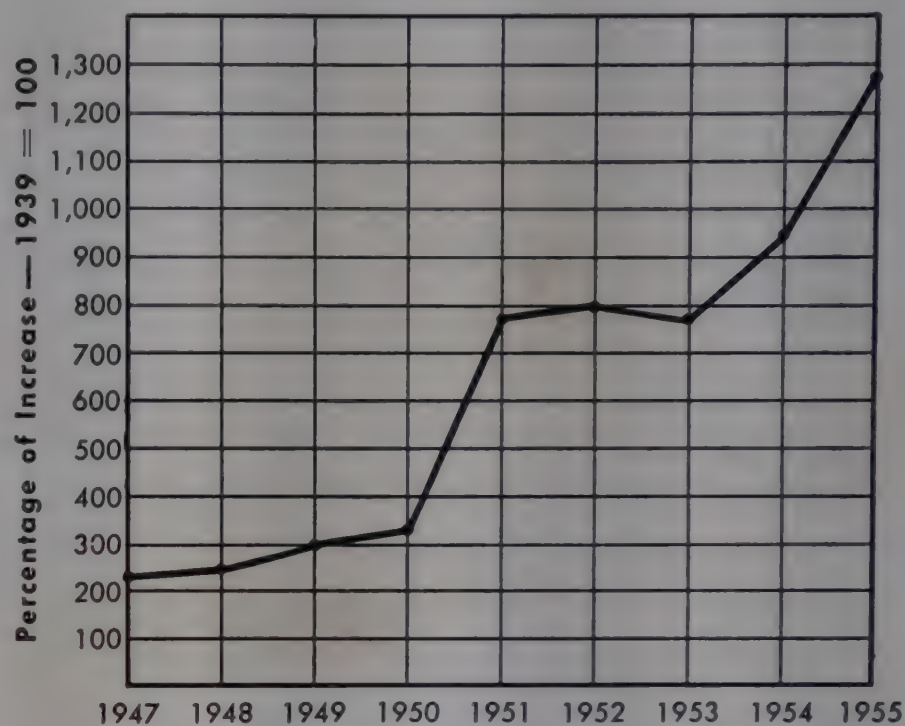
Another important property of tantalum is its ability to immobilize residual gases in electronic tubes, helping to maintain the high vacuum necessary for efficient tube operation. Tantalum has other properties which make it a desirable material in electronic tubes, notably its high melting point, low vapor pressure, low thermal expansion, ductility, and weldability. It has become established as a material for plates and grids in many types of electronic tubes, especially those used at ultrahigh frequencies.

Another distinctive property of tantalum is its ability to form anodic films of unusual stability. This action, combined with immunity to the corrosive action of electrolytes, is the basis for the use of tantalum in electrolytic rectifiers, arresters, and capacitors.

In surgical practice, tantalum is used in sutures, as a mesh in hernias for reinforcing the abdominal wall, and as skull and bone

plates. The metal has no irritating effect upon body tissues, and these will consequently adhere to and grow over tantalum. In the form of wire of 0.003-inch diameter, tantalum has also been employed as an aid to nerve repair.

Among tantalum compounds, tantalum carbide, tantalum pentoxide, and potassium tantalum fluoride are of commercial importance. The carbide has been used with tungsten carbide to impart toughness and a low coefficient of friction to hard carbide tools. Tantalum pentoxide is a principal ingredient in silica-free optical glass of high refractive index. The double fluoride salt is used in the preparation of a catalyst which is used in production of synthetic rubber. Alloys containing iron, tan-



Sales of tantalum and tantalum products

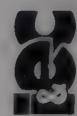
talum, and niobium are used in austenitic stainless steels to inhibit intergranular corrosion, and as an alloying component in certain special purpose steels.

Element occurs in over 40 minerals

Tantalum occurs as the pentoxide in more than 40 minerals (8). It is normally extracted only from tantalite and columbite. Tantalite is a black mineral crystallizing in the orthorhombic system, and may contain as much as 70% of the pentoxide. Tantalite is mined principally in Africa, Australia, and South America. Minor deposits are found in other areas.

The mineral is a tantalate and niobate of iron and manganese. When tantalum pentoxide predominates in the mineral, the common name tantalite is used. When niobium is predominant, the mineral is called columbite. Rocks containing tantalum ores are dikes or tubular bodies that were injected into fissures while in a molten state. Rocks which form the dikes are known as pegmatites, and minerals contained in them are said to belong to the pegmatite assemblage. When mining tantalite in this manner, the vein is followed, but operations may proceed for days, even months, without recovery of any valuable mineral. However, when a pod is finally found, it may contain several hundred pounds of high-grade mineral. Very often, the dikes have been eroded by nearby streams and the minerals are mined from alluvial deposits. Alluvial mining is fairly common in Nigeria and in the Belgian Congo.

Fansteel has long encouraged and sponsored the search for tantalum deposits in all parts of the world. Originally, Fansteel's ore came from one tantalum producing mine in Western Aus-



PLANT PROCESS SERIES

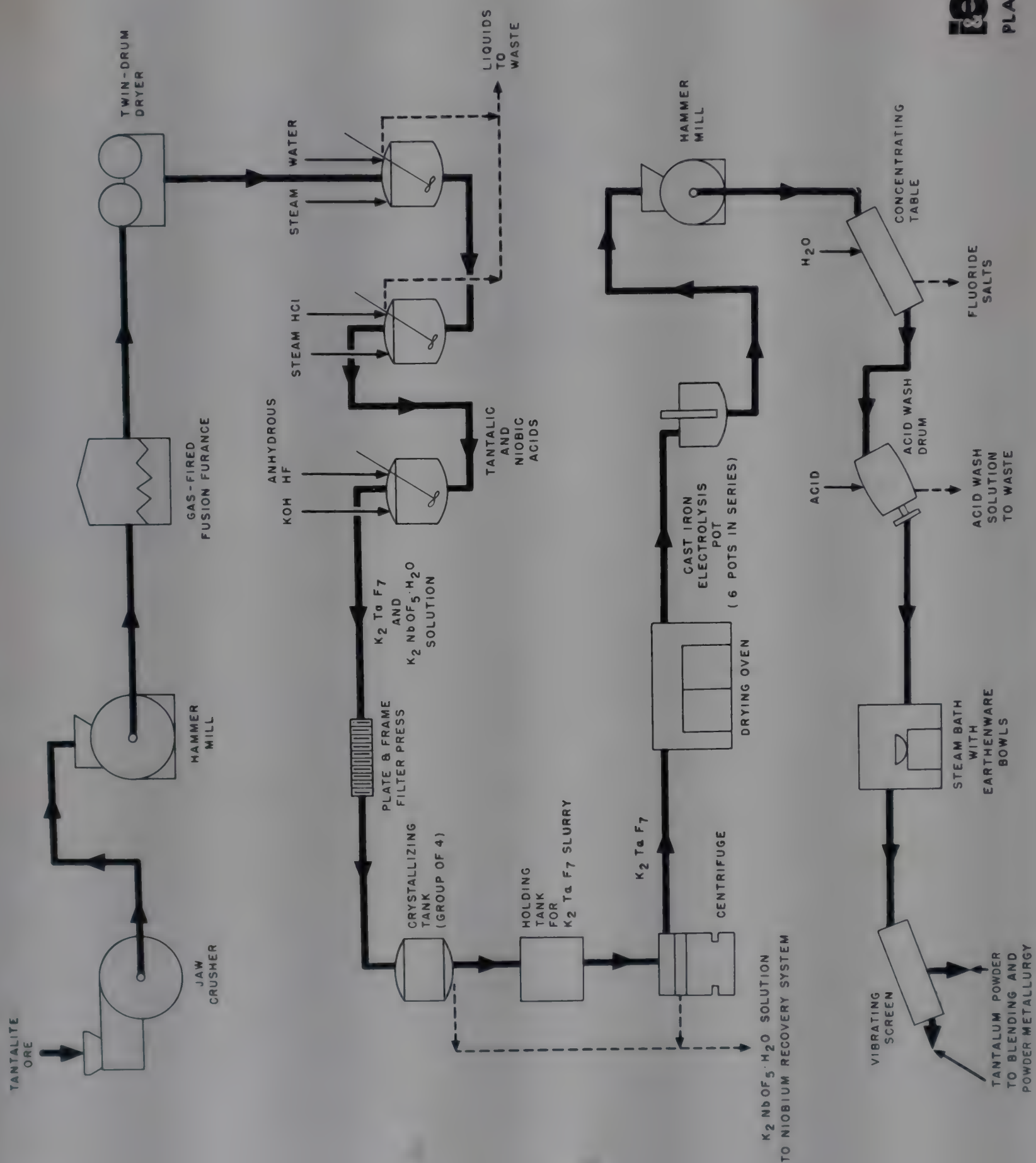


Figure 1. Flow sheet for production of tantalum at the Fansteel Metallurgical Corp., N. Chicago, Ill.

Tantalite Imported for Consumption in United States, by Countries, in Pounds (13)

Country	1944-8 (Av.)	1949	1950	1951	1952	1953
Anglo-Egyptian						
Sudan	20
Argentina	1,861
Australia	8,082	1,467	1,590	20,541
Belgian Congo	297,372	38,086	211,433	210,402	236,701	507,282
Belgium-						
Luxembourg ^a	640	...	85,683	20,876
Brazil	137,519	63,478	13,378	...	49,813	39,532
Canada	140
French Guiana	10,987
India	488
Japan ^a	10,691
Malaya	2,087	3,639
Mozambique	950
Netherlands ^a	...	29,500
Nigeria	14,417	4,480	7,543	5,700	2,273	...
Portugal	35,428	154,323
Southern						
Rhodesia	9,320	233	8,163
Spain	741	...
Sweden	4,242
Uganda	3,725	2,050
Union of						
South Africa	909	1,120	2,036
Total, pounds	475,443	136,664	328,728	238,445	328,866	752,795
Value, \$	384,949	237,292	244,205	190,383	398,849	1,208,134

^a Probably country of transshipment rather than original source.

tralia. The company now obtains its ore primarily from the Belgian Congo.

To encourage increased production of tantalite concentrates, the Defense Materials Procurement Agency announced a government guaranteed purchase program in 1952. The program included an incentive bonus. Fansteel was designated as purchasing agent, and in 1953, Wah Chang Corp. in New York, and the Emergency Procurement Agency, General Services Administration, were named as additional purchasing agents. High grade tantalite (60% Ta₂O₅) brought \$8.00 per pound of tantalum pentoxide to producers. The program was terminated in 1955 after 15 million pounds of pentoxide had been purchased.

For its own use, Fansteel pays an average of \$5.00 per pound for tantalum pentoxide contained in ore concentrates.

Process is refinement of original method

The basic tantalum process was developed by Balke, and the process currently used at Fansteel is a refinement of this basic procedure. Details of the ore separation depend somewhat on the values of other materials, such as cassiterite, that are to be recovered. The ore may contain titanium, silicon, and other impurities. In the manufacturing process, washing, tabling, and magnetic separations are used to isolate tantalite-columbite from minerals associated with it in pegmatite or other formations. (Ores that are processed for use as alloys in the steel industry are normally converted into ferro-niobium-tantalum by reduction in electric furnaces.)

At Fansteel, the ore concentrate arrives in cloth bags and steel drums. Each bag or drum may contain 75 to 150 pounds of concentrate, depending on tantalum content. Prior to processing, the concentrate is stored on pallet skids in a steel warehouse. Electric trucks transport the concentrate to the tantalum manufacturing plant. The ore concentrate is first put through a jaw-crusher (13E), where it is reduced to a particle size of 1/2 inch or

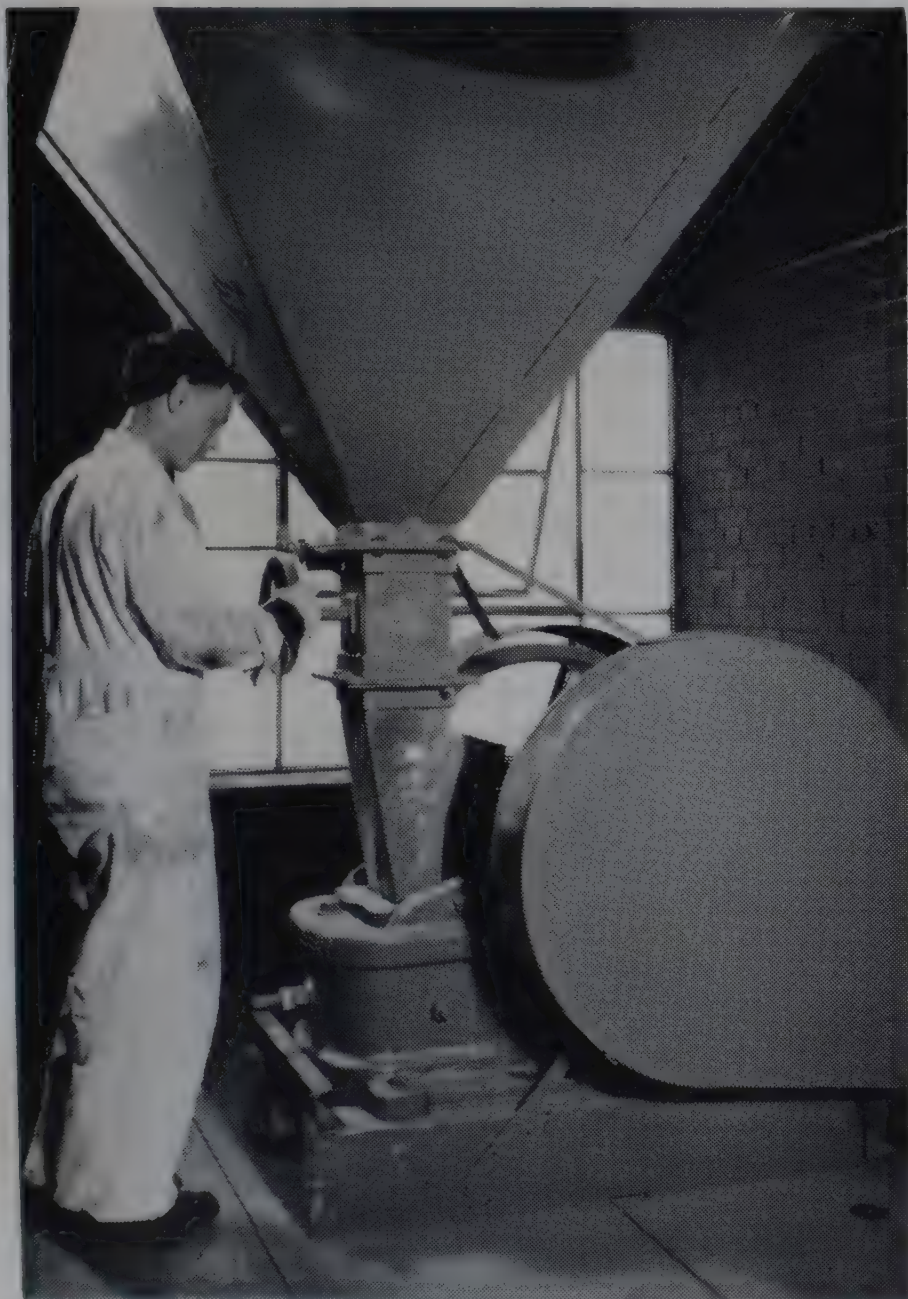
less. After crushing, the product is carried to a hammer mill (6E) equipped with tungsten carbide tipped hammers, and pulverized. The pulverized (about 200 mesh) tantalite-columbite ore concentrate, containing between 20 and 70% tantalum pentoxide, is put into a continuous fusion furnace, and fused with sodium hydroxide.



Tantalum ore storage

The fusion furnace (14E) is propane gas-heated and is equipped with a continuous proportioning feed. Enough solid sodium hydroxide is added to make a molten fusion product. The amount of alkali used, as well as the amount of all other reactants used in the process, always depends upon the tantalum content of the concentrate. Fusion takes place at 1800° F., and produces crude sodium tantalates and niobates.

The molten fusion product (crude sodium tantalates and niobates) discharges onto a drum dryer (4E) to produce an easily handled product. After cooling and solidifying on the twin drums, the crude sodium salt flakes are put into steel drums as they are scraped off the dryer. The drums are taken by elevator to the top floor of the building for further processing.



Pulverizing ore in hammer mill

Beginning with the next operation, leaching, all subsequent chemical operations for tantalum production at Fansteel make use of gravity flow of solutions. Equipment in the three-story plant is arranged in such a manner that each succeeding step is performed one floor lower than the preceding operation.

Batches of about 1/2 ton of the flaked fusion product are dumped into a 2200-gallon rubber-lined steel tank (1E) on the third floor. Hot water and live steam are continuously added to the agitated tank, and all water soluble material is removed by a rubber siphon and pumped into the waste system. Live steam serves to increase agitation as well as to heat the mixture. When all water soluble material is removed, the crude salt mixture or mud is washed with hot, dilute hydrochloric acid. Live steam plays the same role here as in water leaching. Acid solu-

ble impurities are also removed with a rubber siphon and pumped into the waste system. Acid leaching gives a white mixture of tantalic and niobic acids.

Tantalum and niobium separated by crystallization of fluoride salts

Anhydrous hydrogen fluoride is next metered into the tank to dissolve the tantalic and niobic acids. The hydrogen fluoride is stored in a steel tank which has a capacity of two railroad tank cars. The storage tank is refilled whenever its contents drop below the capacity of one tank car. Piping connecting hydrogen fluoride storage and the processing tanks is made of welded steel.

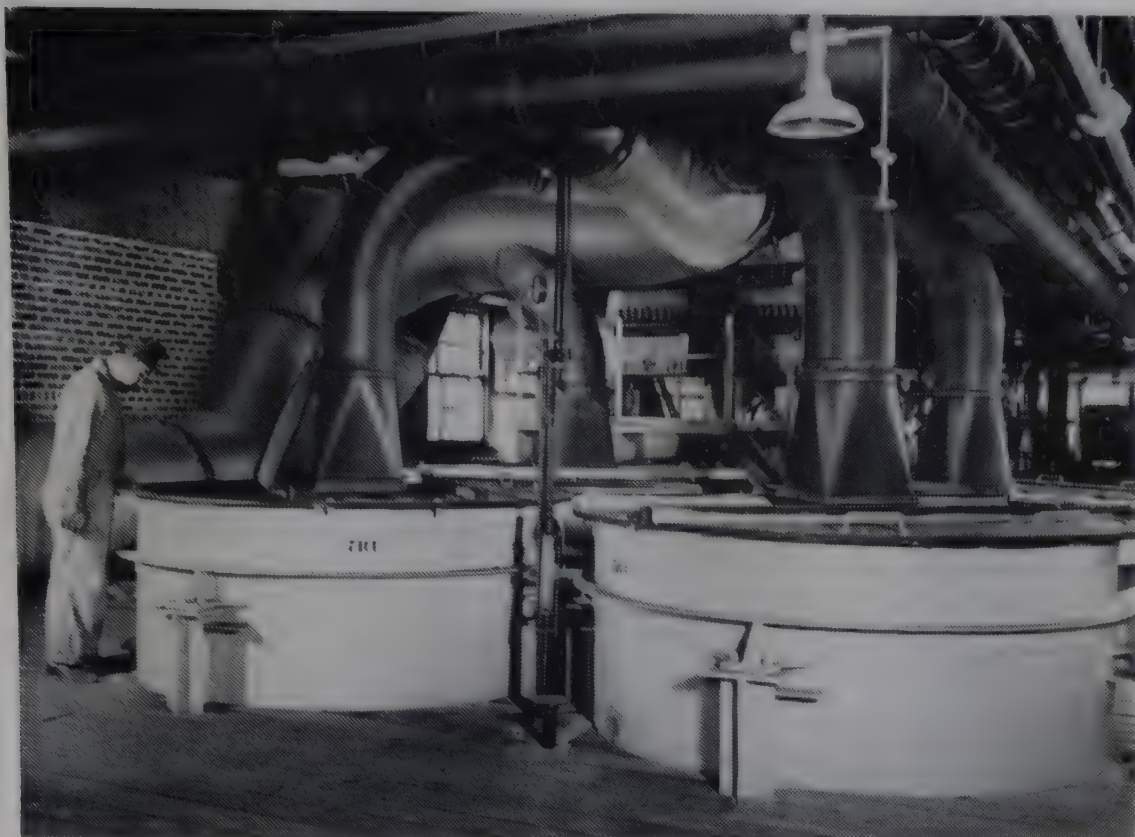
Until earlier this year, 70% hydrofluoric acid was used in this step. The acid was stored in steel drums, and the drums were put up on racks as needed. Hard-rubber piping was used to transfer the aqueous acid from the drums to the tanks. Anhydrous hydrogen fluoride has increased the safety, efficiency, and economy of the operation. Savings figures on the new technique will be available after the system is in operation for a few months.

When the acid solution step is complete, aqueous potassium hydroxide is added in stoichiometric amounts, giving a solution of potassium tantalum fluoride (K_2TaF_7) and potassium niobium oxyfluoride (K_2NbOF_5). The hot solution flows by gravity to a wood plate-and-frame filter press (12E) equipped with canvas and Orlon to remove impurities. The filtrate flows into hard rubber-lined steel crystallizing tanks (1E) on the floor below.



Men with specially designed clothing unload tank car of anhydrous hydrogen fluoride

Crystallization is allowed to take place naturally. Complete separation of potassium tantalum fluoride from the solution sometimes requires several days. No attempts to speed the process are made. When crystallization is complete, the mother liquor, containing potassium niobium oxyfluoride, is removed with a rubber siphon and pumped to the niobium recovery system. (The mother liquor is concentrated, and another crop of tantalum double fluoride crystals, containing some niobium, is recovered.



In a special crystallizing arrangement designed by Fansteel engineers, the four crystallizing tanks are arranged in two parallel pairs. Each tank has a capacity of 2500 gallons, and is connected at the bottom to a central rubber-lined steel holding tank (1E) on the first floor.

The fume disposal system consists of five gas-washing towers (11E), each having a capacity of 30,000 to 34,000 cubic feet per minute. The fumes are washed with 2 to 6% sodium hydroxide solution before escaping into the outdoor atmosphere. A positive air pressure is maintained in the plant at all times.

The niobium is recovered from the mother liquor as sodium niobate by the addition of sodium hydroxide.) The tantalum fluoride salt slurry remaining in the bottom of the crystallizing tanks

is then allowed to flow by gravity into the holding tank.

The fractional crystallization process is based on the different solubilities of the double fluoride salts of tantalum and niobium. At room temperature (20° C.), the solubility of potassium tantalum fluoride (K_2TaF_7) is 7.5 grams per liter. At the same temperature, the solubility of potassium niobium oxyfluoride ($K_2NbOF_5 \cdot H_2O$) is 91.5 grams per liter.

The potassium tantalum fluoride slurry from the holding tank is centrifuged (15E) at 5000 r.p.m. in a 36-inch rubber-covered suspended basket. About 770 pounds of salt are fed into the centrifuge at one time. Mother liquor from the centrifugation is routed into the niobium recovery system. The tantalum salt removed from the centrifuge is spread on wooden trays with Masonite bottoms, and dried in a steam-heated drying oven (8E). Dry potassium tantalum fluoride is stored in fiber drums to await electrolysis. Yields of the salt vary with the tantalum pentoxide content of the original concentrate, but are generally in the range of 90%.

Element obtained by chemical reduction or by electrolysis

Tantalum metal can be obtained by sodium reduction of potassium tantalum fluoride, the reduction of tantalum chloride by hydrogen (9), or by electrolysis.

Sodium reduction is carried out in steel containers. Alternate layers of the fluoride salt and of sodium metal are placed in the container which is closed with a loosely fitting lid. Application of heat initiates an exothermic reaction. After cooling, the mass is pulverized and extracted with water. The tantalum powder remaining is washed with dilute acid to remove impurities, and is then dried.

Potassium tantalum fluoride crystal growth in tank





Tantalum metal powder mixed with residues is washed out on the concentrating table, then with acids

Hydrogen reduction of the chloride has been used for coating base metals with tantalum, but not for production of powder for subsequent processing into massive metal. In the procedure, a stream of pure hydrogen is passed over tantalum chloride and the mixed gases are brought into contact with a heated base metal. Porosity can be eliminated by applying two or three overlapping coats, burnishing each coat, and shifting the specimen within the plating apparatus before applying the next plate.

In the Fansteel process, tantalum metal is obtained from potassium tantalum fluoride by electrolysis. Tantalum is deposited in the form of a cake consisting of crystalline aggregates. A series of six pots has a capacity of 88 to 110 pounds of tantalum, and each electrolysis cycle requires 14 hours.

After cooling at room temperature, the tantalum cake is removed from the pots and pulverized in a hammer mill (6E). The pulverized tantalum is washed with water on a concentrating table (7E) to remove fluoride salts. At the same time, very coarse and very fine powders are separated. Water washed tantalum powder is carried to acid wash drums (2E, 5E) for washing with strong acids. Tantalum metal from the acid wash is placed in stoneware dishes, and dried on a Fansteel-made steam bath. At this stage, the powdered tantalum is 99.8% pure.

An acid mixture, such as aqua regia, can be used in the operation. The drums are made of rubber-lined steel, and are equipped with Teflon steam injectors.

The dry powder is then screened, graded, and blended. Blends are used for one of the following:

1. Ingots for bar or sheet
2. Ingots for rods and/or wire
3. Powder for use in capacitors

Particle size of the blends depends upon eventual use.

Powder metallurgy lends a hand

For the preparation of ingots, tantalum powder is pressed into bars 24 or 30 inches long, and up to 1 square inch in cross section. For production of wire or rod, a square bar is used. For sheet, a wider and thinner bar is preferred. The powder is pressed into

fragile, chalklike ingots by a 3000-ton press (3E), which applies stress in three directions in order to obtain uniform pressure.

Sintering in vacuum (9E, 10E) converts the tantalum into massive metal. Sintering is done in vacuum furnaces designed and built by Fansteel. The tantalum bars from the press are held between water-cooled terminals in the furnace, and heating is accomplished by passing an electric current through the bar. After sintering, the bar, which has a density of about 90% of



The electrolytic system, designed and built by the Fansteel staff, consists of 6 removable cast-iron pots placed in series, on copper conducting plates. Power is obtained from a 440-volt alternating current source, which is converted to direct current in motor-generator sets. Potassium tantalum fluoride is scooped into the pots with a rubber dipper. The salt is the electrolyte in the process, the pot is the cathode, and a graphite rod serves as the anode. Salt is added to each pot during electrolysis as the reaction progresses, until the pot is filled with metallic tantalum.

Drying tantalum powder in stoneware dishes over steam bath



theoretical, is rolled or forged and again heated. The final product is massive metal of high density and essentially zero porosity.

Working of ingots into sheets or rods and wire is carried out by conventional methods. All working of tantalum is done cold. After a reduction of 70 to 80% in thickness, the metal is annealed in a vacuum to facilitate further working. Sheet down to 0.0005 inch in thickness is produced commercially, and thicknesses as low as 0.0002 inch can be made. Rod and wire are fabricated by rolling, and then drawing in carbide and diamond dies, the latter for smaller sizes. Tantalum sheet can be formed, deep drawn, or spun without difficulty.

Fansteel also has a process for recovering tantalum from scrap. In this process, clean tantalum scrap is hydrogenated in company designed equipment. The product is pulverized in a hammer mill and vacuum degassed, resulting in tantalum powder of high purity. Massive metal can be made from the recovered tantalum, or it can be used in powder form.

Plant runs 24 hours a day

The Fansteel plant is operated 24 hours a day, every day of the year. A staff of 75 operators and supervisors is assigned to the production of tantalum.

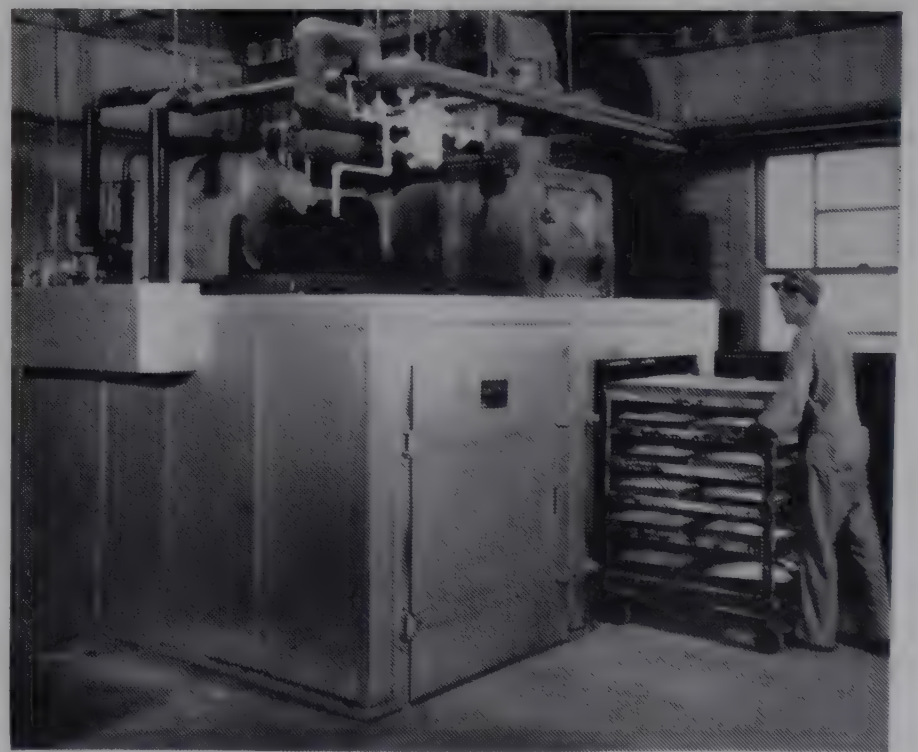
As a precaution against the possibility of contamination, none of the equipment in the tantalum processing line is used for any other purposes. Impurities from corrosion are the greatest concern, necessitating almost complete corrosion-proofing of equipment. To date, Fansteel has not had any serious problems in this respect. This is partly because so much of the processing equipment is of company design and manufacture. Rubber is used extensively, particularly in tanks and piping. No difficulties in piping have been encountered, and tanks are relined or patched when necessary.

Unusual precautions have been taken throughout the plant to avoid the presence of fumes and dust in the atmosphere. Wood floors are laid so that there is about one inch of space between planks, eliminating the possibility of gas pockets. All the processing tanks in the plant are covered and equipped with ducts for fume removal.

Liquid wastes are discharged into a stoneware lined holding tank, neutralized, and discharged into a nearby creek.

Control analysis is essential

Since every step in the process depends on the amount of tantalum present, and impurities must be avoided, a rigid control system is in operation. When the expense of the initial ore is considered together with the added expense of processing, it is not surprising that more than one half of the technical people employed by Fansteel serve as policemen for the process.



Drying of the potassium tantalum fluoride crystals

Spectrographic analysis is used extensively. All ore concentrate lots are analyzed immediately upon receipt. All reagents used in the process undergo analysis. Tantalum content is



An important feature of Fansteel's sintering scheme is the flexible electrical arrangement of the furnaces. Furnaces may be connected six or three in a series, or singly. Current is applied in increasing amounts during the operation. Each lot of tantalum that undergoes sintering is identified by stylus numbering applied to the ingots by the press operator. After sintering, the number is stamped with a die. Weight of each ingot is 6.6 to 15.5 pounds, again depending on end use.

determined in all lots of potassium tantalum fluoride and tantalum powder produced. If, at any time, spectrographic analysis shows a variation from specifications, standard wet methods of analysis or x-ray studies are employed to confirm the initial findings.

Powdered tantalum also undergoes particle size and distribution determinations. Bars are put through hardness, tensile strength, and density tests.

Future tantalum production

Increasing use of tantalum has underlined the fact that the United States is dependent for tantalum ore on deposits outside its own boundaries. Domestic production of ore was less than 0.2% of the world's total in 1953 (12). Because of the strategic importance of tantalum, the Government includes tantalite-columbite ores in the National Stockpile. Total supply of tantalum in all forms in the United States amounted to 1.5 million pounds in 1953.

Domestic potential reserves of tantalite and columbite have increased somewhat with the discovery of niobium and tantalum-

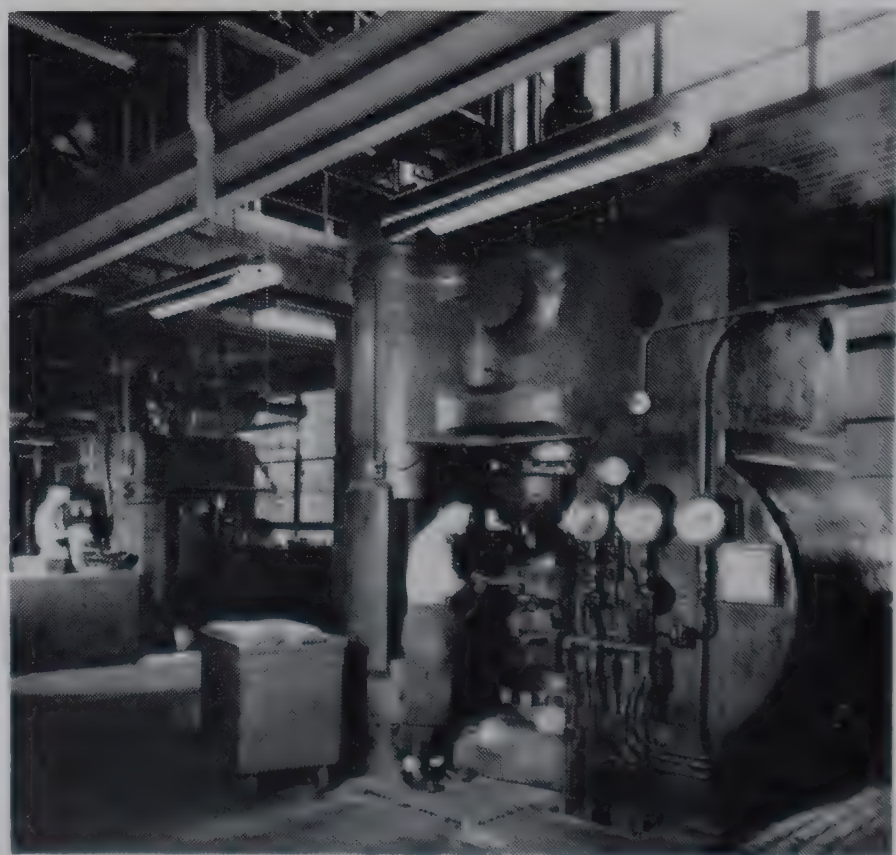
containing minerals in deposits in Idaho and in the southeastern states. Tantalite reserves in the United States in 1953 were estimated at 130,000 pounds, compared with foreign reserves of over 30 million pounds (12).

Recovery of tantalum and niobium from slag from tin smelting also has been proved successful (12). Concentrates from open-pit pegmatite tin mining in the Belgian Congo are dried and treated magnetically to remove tantalite and columbite. About 65 to 75% of the combination is recovered in a concentrate containing 65 to 75% of combined tantalum and niobium pentoxides. The remaining tantalum and niobium is in the final slag obtained from tin smelting, and is shipped to the United States for refining. As a result, the metallic oxides concentration of imported slag is the same as that of the ore, previously the only source of supply.

Recent research efforts on tantalum have been devoted to devising new schemes for separating tantalum and niobium (10).

Separation of tantalum and niobium by liquid-liquid extraction has been proved feasible by several investigators. Both metals are extracted from hydrofluoric-hydrochloric acid solutions by aliphatic and aromatic ketones (14), but the equilibrium distribution favors the extraction of tantalum. The system hydrofluoric acid-hydrochloric acid-methyl isobutyl ketone has been used in the production of high purity tantalum and niobium oxides. Continuous countercurrent runs were performed in a 12-foot perforated-plate pulse column. Normal tantalum and niobium, as well as their radioactive tracers, were employed to show that the separation of niobium from tantalum was quantitative by

liquid-liquid extraction of their hydrochloric acid solution with long chain aliphatic and aromatic amines in organic solvents (4).



Compacting tantalum ingots in hydraulic press



Schneible fume disposal towers

Additional results indicate that sulfate and oxalate complexes of tantalum and niobium can be extracted with solvated amines. Amine systems should prove useful in industrial separation operations (10).

Feasibility of using 12*N* hydrochloric acid for preferential extraction of tantalum from mixed aliphatic and aromatic ketone solutions containing anhydrous tantalum and niobium pentachlorides has been shown (15). Relatively pure oxides were prepared using the system isobutyl ketone-diisobutyl ketone-12*N* hydrochloric acid. Possibilities of extraction on a commercial basis are enhanced by the presence of ferric chloride in the system.

Tantalum sponge metal has been produced on a laboratory scale by the Bureau of Mines (7). In this procedure, tantalum chloride was reduced with magnesium in an inert atmosphere (Kroll process).

Fansteel itself is currently in the middle of a \$1-million expansion program for tantalum and niobium.

Other metals produced

In addition to producing tantalum and niobium, Fansteel also produces tungsten and molybdenum. The two metals are used for electrical contacts, particularly in automotive ignitions, vibrators, telegraph relays, and other devices where contacting parts are in practically continuous service. Both tungsten and molyb-

denum are used as heating elements in electric furnaces where working temperatures of 1600° to 2000° C. are required.

The company also makes electrical contacts from silver, tungsten, molybdenum, and metals of the platinum group. Selenium rectifiers, refractory metal carbides, and resistance welding materials are other products.

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- (14) Werning, J. R., Higbie, K. B., others, *IND. ENG. CHEM.* **46**, 644-52 (1954).
- (15) *Ibid.*, pp. 2491-8.

Processing equipment

- (1E) American Hard Rubber Co., 87 Worth St., New York, N. Y., rubber-lined tank.
- (2E) Baird Machine Co., Stratford, Conn., acid-wash drums.
- (3E) Baldwin-Lima-Hamilton Corp., 940 Simpson St., Eddystone, Pa., hydraulic press.
- (4E) Buflovak Equipment Div. of Blaw-Knox Co., 43 Winchester Ave., Buffalo, N. Y., twin-drum dryer.
- (5E) Casalbi Co., Jackson, Mich., acid-wash drums.
- (6E) Combustion Engineering-Superheater, Inc., Raymond Pulverizer Div., 1318 N. Branch, Chicago, Ill., hammer mill.
- (7E) Deister Concentrator Co., Glasgow and Wayne St., Fort Wayne, Ind., concentrating table.
- (8E) Drying Systems, Inc., 1808 Foster Ave., Chicago, Ill., steam-heated drying oven.
- (9E) Kinney Manufacturing Div., New York Air Brake Co., 3535 Washington St., Boston, Mass., oil diffusion vacuum pumps.
- (10E) National Research Corp., 160 Charlemont, Newton Highlands, Mass., oil diffusion vacuum pumps.
- (11E) C. B. Schneible Co., 210 Stephenson Bldg., Detroit, Mich., fume disposal towers.
- (12E) D. R. Sperry & Co., Batavia, Ill., plate-and-frame filter press.
- (13E) Sturtevant Mill Co., 1 Harrison Square, Boston, Mass., jaw-crusher.
- (14E) Sunbeam Corp., Industrial Furnace Div., 4401-53 Ogden Ave., Dept. 113, Chicago, Ill., gas-fired fusion furnace with continuous proportioning feed.
- (15E) Tolhurst Centrifugals Div., American Machine & Metals, Inc., 48 Thomas St., East Moline, Ill., centrifuge.

Note: This article appeared in Industrial and Engineering Chemistry in April, 1956



Granulated Fertilizers By Continuous Ammoniation

HARRY W. HAINES, JR., Associate Editor

in collaboration with

FREMONT LANGE

Ark-Mo Plant Food Co., Walnut Ridge, Ark.

FERTILIZER production in the United States is far from being a slow moving industry, both in technology and output. It is a dynamic business, where consumption more than doubled during the past 10 years (8), in terms of primary plant nutrients. Faced with keen competition, producers constantly search for ways to improve product quality at lower cost to the farmer, whose income has declined steadily since the close of the Korean War.

Mixed fertilizer continues to be the principal form of fertilizer used by the farmer, supplying about 70% of the fertilizer he consumes. In recent years the farmer has been buying this material in more concentrated doses. The plant food content in mixed goods has climbed steadily upward to a national average of about 28%, contrasted with 20% in 1940. In some areas the trend toward high-analysis materials is much stronger; the West North Central states in 1953-54, for example, used mixed fertilizers containing an average of 35% plant nutrients (16). (Mixed goods may contain all three plant nutrients: nitrogen, available phosphate as P_2O_5 , and potassium expressed as K_2O . One unit is equivalent to 20 pounds of plant food. All materials which contain a total of 33 units or more per ton are considered as high-analysis materials.)

Especially significant from the technological viewpoint is the rapid change to granulation in the past few years, a trend that has taken place along with increased use of high-analysis materials.

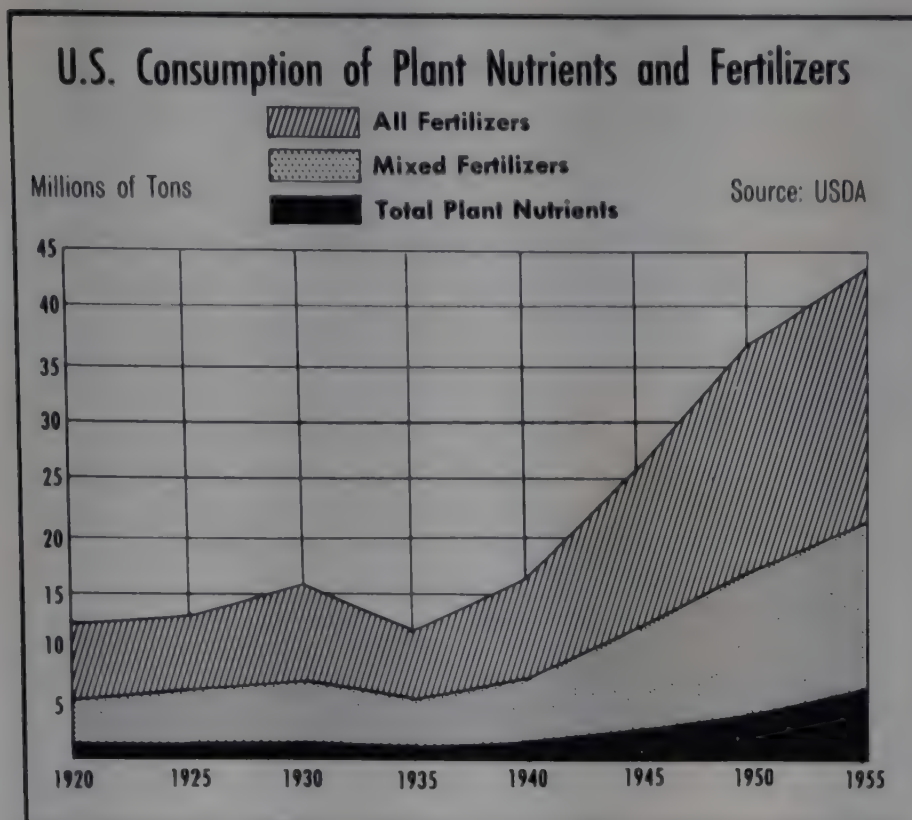
More than 80 of some 1200 fertilizer mixing plants now produce granular products. At the close of 1955, the nation's capacity of granular products exceeded 2,000,000 tons annually, 12% of the total production of mixtures (4).

One reason for the trend toward granulation is that most high-analysis fertilizers are likely to cake unless processed in this form. Granulated products add greatly to the farmer's convenience, making more uniform distribution in the field

Plant Food Content of Mixed Fertilizers^a

Year	Per Cent			
	N_2	K_2O	P_2O_5	Total
1920	2.30	2.40	9.20	13.90
1925	2.50	4.10	9.40	16.00
1930	3.10	5.00	9.80	17.90
1935	3.49	5.51	9.32	18.32
1940	3.76	6.50	9.64	19.90
1945	3.96	7.51	10.27	21.74
1950	4.06	8.52	11.00	23.58
1955	5.40	10.60	11.70	27.70

^a Source, USDA.



easier, while decreasing dust losses. And granulation prevents segregation of fertilizer ingredients, assuring a more balanced diet for crops (8).

When groups in this country began to study granulation, ammoniation of superphosphate was common practice, although conducted as a batch operation. And until recently most plants practiced a low degree of ammoniation. Three years ago, TVA developed a continuous ammoniator that would produce high-analysis mixtures (25, 26). This equipment proved to be an excellent means of granulation. Today, 57 companies have been given a royalty-free license to use or manufacture the continuous ammoniator. Among the first to use the new unit was the Ark-Mo Plant Food Co. which started up its unit at Walnut Ridge, Ark., on March 7, 1955 (17).

Chemistry enters the field

Although fertilizer technology has been classified for many years as a chemical process, it was until recently primarily a mechanical operation. Chemists and chemical engineers were conspicuously absent from many fertilizer manufacturing facilities.

Until 1928, when ammoniation of superphosphate became an integral part of mixed fertilizer production, manufacturers treated phosphate rock with sulfuric acid to make superphosphate, then blended superphosphate with potash salts and organic materials to produce various formulations.

Ammoniation of superphosphates increased slowly at first. As recently as 1940, the industry consumed only 60,000 tons of nitrogen annually in the form of ammonia and nitrogen solutions. Last year, consumption exceeded 500,000 tons—about 24% of the total nitrogen used as fertilizer.

Ammonia and ammoniating solutions (which contain ammonia along with ammonium nitrate or urea) are the cheapest forms of nitrogen available to the fertilizer manufacturer; in the interest of economy he has adapted them quickly to their use. They are also highly concentrated materials; they facilitate preparation of high-analysis fertilizers. The extent to which superphosphate can be ammoniated imposed a limitation on the amount of ammoniated solutions that could be incorporated in mixtures. Many manufacturers now add sulfuric or phosphoric acid to make the mixture absorb more ammoniating solution. This practice, increasing rapidly in recent years, has placed additional emphasis on the chemical aspects of mixed fertilizer production.

When ammonia reacts with superphosphate (water soluble phosphoric acid and monocalcium phosphate), the heat of reaction may liberate moisture with possibility of caking. Equations for the principal ammoniating reactions have been published by Keenen (11) and by White, Hardesty, and Ross (24):



Ordinary superphosphate, however, contains calcium sulfate. This raw material leads to this set of reactions:



Calcium sulfate is virtually absent from concentrated superphosphate. If this type of superphosphate has been used as the raw material, still other reactions take place:



Practical degrees of ammoniation with ordinary and concentrated superphosphate, respectively, are approximately six and four pounds of neutralizing ammonia per unit of available phosphorus pentoxide (25) (the maximum rate of ammoniation without serious reversion of phosphorus pentoxide to a citrate in soluble form). Most mixtures are formulated so that five pounds of neutralizing ammonia reacts with one unit of phosphorus pentoxide (3).

From batch to continuous operation

In its simplest form, mixed fertilizer production is a batch process for bringing together in their proper proportions the plant nutrients available to fertilizer manufacturers. The conventional plant in this country uses such raw materials as normal superphosphate, triple superphosphate, anhydrous ammonia, nitrogen solutions, ammonium sulfate, and potassium chloride. With the increasing demand for granulated fertilizers, many conventional mixers are endeavoring to install granulation equipment. Limited budgets are the rule rather than the exception; most granulation equipment consists principally of a rotary dryer and cooler, together with conventional auxiliary equipment, and screens for sizing the product. The granulated fertilizer is packaged in 80- to 100-pound bags for shipment.

Where one can afford to do so, it is best to have a plant designed to use anhydrous ammonia and ammoniating solutions exclusively, in place of ammonium sulfate, for introduction of low-cost nitrogen into the mixture (23). By the elimination of ammonium sulfate, it is possible to raise the analysis almost 25%, cut production costs almost \$10 per ton, and at the same time produce a good granular product. A greater proportion of normal superphosphate can be consumed in high-analysis formulations which saves money for the producer who makes his own superphosphate. Further economies may be accomplished with the TVA ammoniator which makes the process continuous instead of a batch operation. The ammoniator also provides a means for better control of composition and physical form of the products.

Ark-Mo Plant Food's installation combines ammoniation and granulation into one step, saving considerable money on initial equipment costs. And the process has definite production economies because granulation is based on operation at low moisture content, to utilize heat from the ammoniating reactions for partially drying the products.

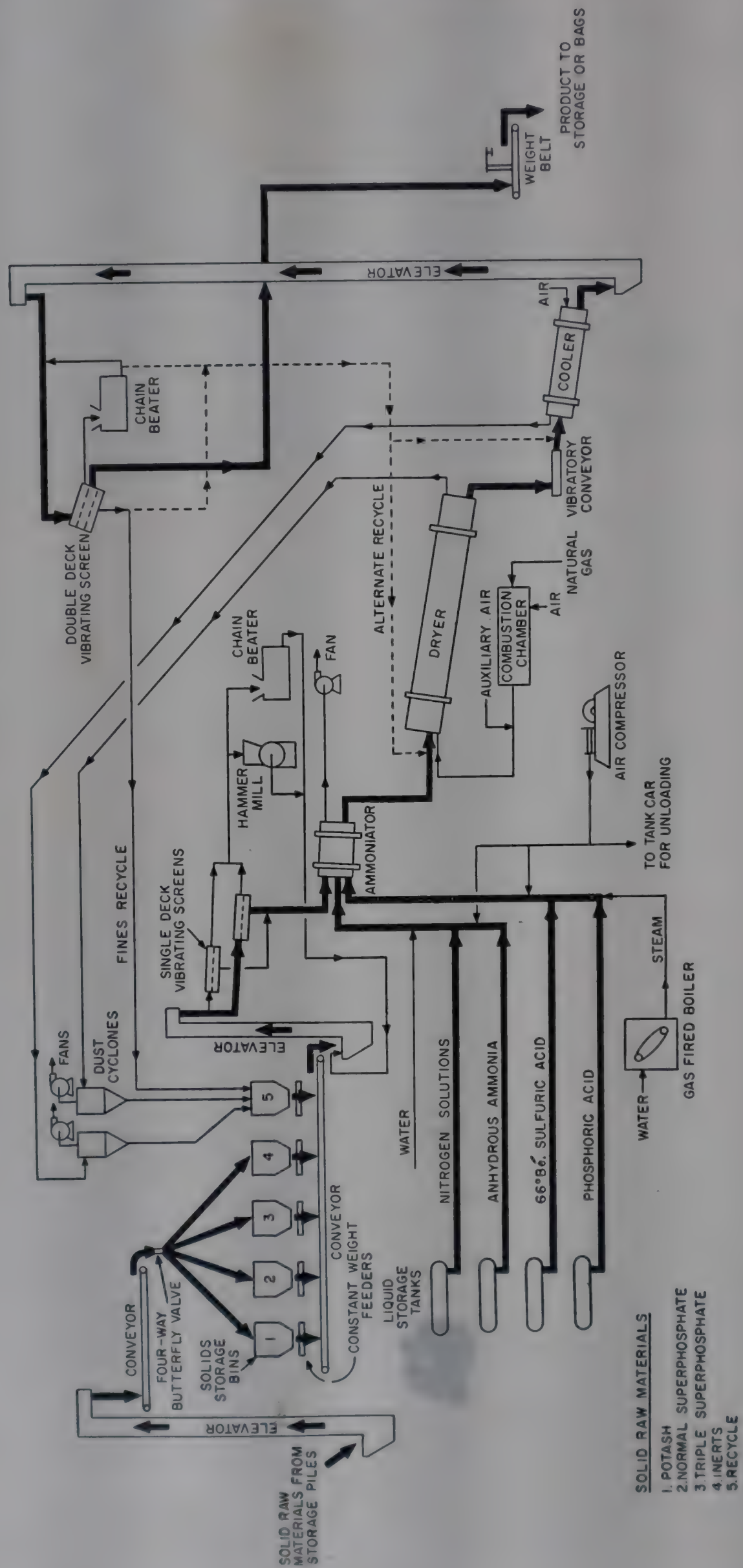


Figure 1. Flow sheet for production of granulated fertilizers by continuous ammoniation by Ark-Mo Plant Food Co., Walnut Ridge, Ark.

Many variables affect granulation

For any material to be granulated satisfactorily, it must be cohesive; some physical means of controlling degree of agglomeration is essential. A number of theories have been advanced as to how various materials and mechanical equipment affect agglomeration, but most investigators generally agree on the important factors.

A liquid phase is necessary to cause plasticity, and moisture content is an important variable (4). Too little plasticity may result in an excessive amount of fines in the system; too much liquid phase causes large masses to form, which eventually become unmanageable. Temperatures and composition of the formulation are also critical factors.

Mixtures containing soluble salts may be granulated at very low moisture content if the operating temperature is high. Then, the proper moisture content is determined to a large extent by the concentration of soluble compounds, and their solubility-temperature relationship.

Ammonium nitrate is the most water-soluble fertilizer, with urea running a close second. The solubility of ammonium nitrate by weight increases from 54% at 32° F. to 89% at 212° F.; the solubility of urea increases from 39 to 87%. At 68° F. their solubilities are 66 and 52%, respectively. Temperature can be a critical factor in producing the correct degree of plasticity when these materials are present. During the drying and cooling steps, low moisture content and a large amount of salts in solution hasten crystallization, contributing to permanency of the granules formed during agglomeration (18).

Formulation itself can be used to some extent for control of granulation. If the manufacturer wishes to granulate at very low moisture content, so that artificial drying is not required, he must often employ temperatures as high as 180° to 250° F. But these temperatures are higher than those usually obtained through ammoniation of superphosphate. As a convenient means of reaching this temperature level, the manufacturer will frequently react additional ammonia with sulfuric or phosphoric acid, which also becomes an economical method for increasing nitrogen content of the mixture. The extent to which this heat of reaction can be utilized depends in part upon heat losses from the ammoniating unit. He may also inject steam or hot water into the reactor.

Equipment that allows great flexibility of operation is indeed important. The industry offers a wide range of grades for sale, and for some of these grades the most economical formula produces either too little or too much plasticity; the mixture is not self-granulating.

Obviously, it is not practical to have reactors or ammoniators that will create optimum conditions for granulation for all of the most economical formulas. A compromise must be made. In formulas containing small amounts of moisture and soluble salts, steam is injected to increase plasticity; in formulas containing large amounts of moisture and soluble salts, cooled product is recycled to decrease plasticity.

Raw material particle size affects the chemical composition and physical properties of the finished product. For a granule to contain the correct amount of each plant food, the particle size of the raw materials must be smaller than the particle size of the finished product. Just as a variety of particle sizes in concrete produces a more durable foundation, the wide range of

particle sizes in most raw materials enhance the formation of durable granules.

The ball starts rolling

Ark-Mo's installation (Figure 1), designed by Spencer Chemical Co. engineers, is essentially a blown-up version of the continuous ammoniating pilot plant (5) developed by TVA personnel (Figure 2).

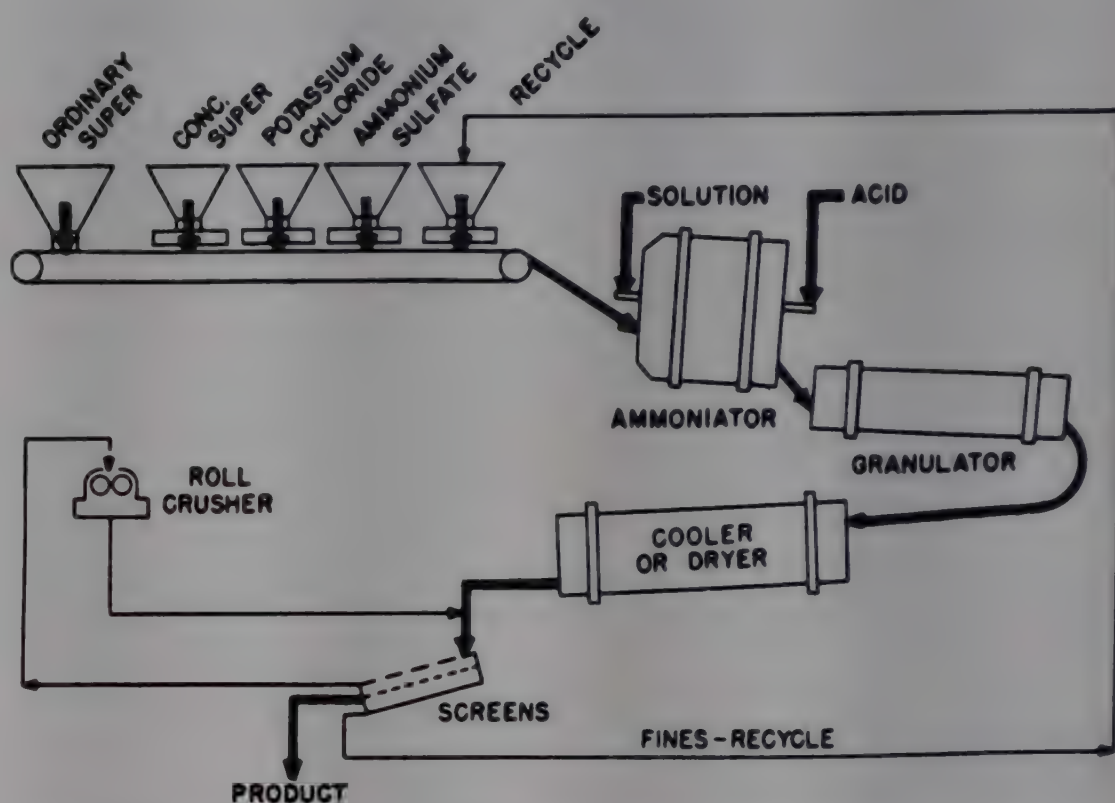


Figure 2. Flow diagram of TVA pilot plant for granulation of high-analysis fertilizers

The TVA pilot plant had a capacity of about 3 tons of granular product per hour (6). Superphosphate, potassium chloride, recycled fines, and any other solid materials required for formulation were fed by volumetric feeders onto a collecting belt and then into the ammoniator.

The TVA ammoniator, 3 feet in diameter by 3 feet long, usually rotated at 15 r.p.m. Bed depth was maintained at approximately 9 inches, which at maximum throughput gave a retention time of about 3 minutes.

Material from the ammoniator flowed through a chute down into the granulator, located on the second floor of the pilot plant area. The granulator, an open cylinder 24 inches in diameter by 6.5 feet long, rotated at 20 r.p.m. Granulated material went to a cooler, 3 feet in diameter by 24 feet long, which contained flights. During normal operation, air flow in the cooler was countercurrent to the flow of solids, and the cooler exit temperature was about 100° F. In a few cases, however, they used the cooler as a dryer, operating it with cocurrent firing.

A set of screens, a crusher, and conveying equipment sized the product to approximately -6 and +28 mesh. Undersized product was recycled to the ammoniator.

In an earlier layout, the TVA pilot plant had both a dryer and cooler, with the dryer preceding the cooler (22). Product fines were recycled to the granulator rather than to the ammoniator.

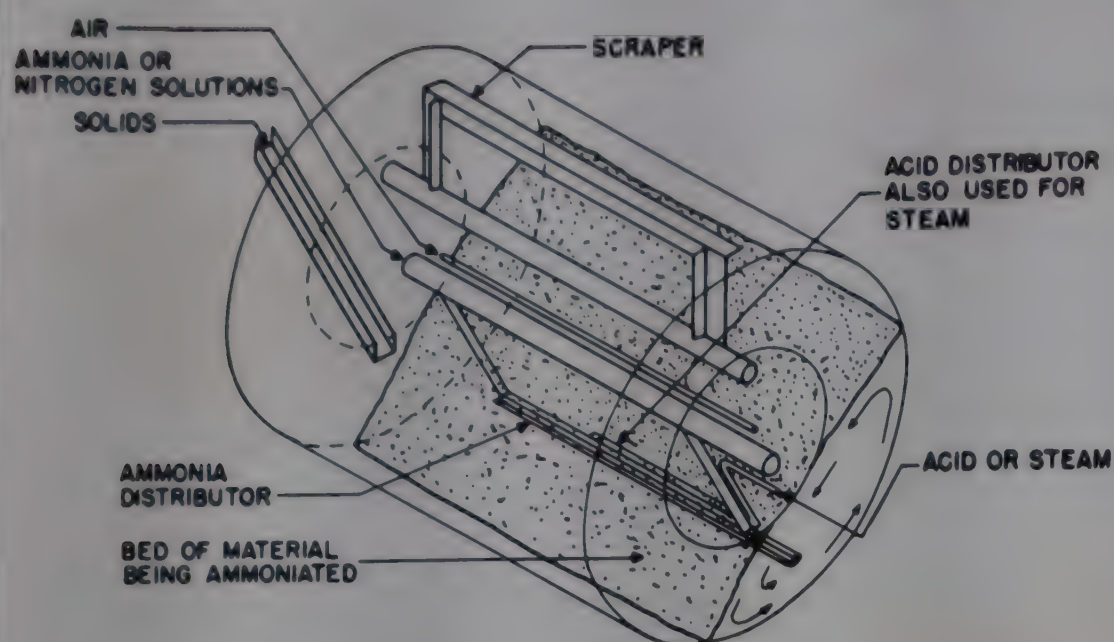


Figure 3. Pictorial view of TVA pilot plant continuous ammoniator

Ammonia or ammoniating solutions, or mixtures of the two, were injected under the bed of material through a specially designed sparger (Figure 3). Sulfuric acid, phosphoric acid, or steam entered through an adjacent distributor. TVA engineers used air for cooling and controlling granule size, and this air was supplied to the ammoniator from a drilled pipe located over the bed of material. (The drilled holes in the pipe were located so as to direct air jets onto the surface of the bed.)

When water was needed for granulation, it was either sprayed on the surface of the bed, or mixed with ammoniating solutions going into the ammonia distributor. An exhaust fan pulled air through the ammoniator to sweep out water vapor and fumes.

Ark-Mo uses solid and liquid materials

By combining ammoniation and granulation in one step, Ark-Mo Plant Food Co. was able to build a 15-ton-per-hour plant for less than \$360,000 (Table I), using a few equipment items salvaged from their previous installation (1). It is designed to handle both solid and liquid raw materials.

Table I. Capital Investment of Granulation Plant

Item	Cost, \$
Equipment	
Dry raw materials handling	47,700
Liquid raw materials handling	16,500
Processing	101,100
Parting agent	7,200
Utility	10,200
Liquid storage	21,600
	<hr/> 204,300
Building	77,900
Labor ^a (24,962 man hours @\$2.00 per hour)	49,900
Engineering	25,000
Total cost	<hr/> 357,100

^a Excluding contract for building siding.

Specifications on solid raw materials must be closely watched. It is possible to manufacture some grades, like 10-10-10 and 14-14-14, with fine potash (Table II), but attempts to make high-potash grades with fine potash have failed. Large particles

serve as a nucleus for the granulated product, whereas fine potash particles stick loosely to the outer surface of the granules. Coarse potash is used in the formulation of 3-12-12, 3-9-18, and 3-9-27 grades. Of the three potash types—recrystallized (white, 100% -28 mesh), flotation (red, 23% +28 mesh), and granular (68% +28 mesh)—significantly better results are obtained with the granular material. Ark-Mo insists on coarse potash in the range of -10 to +30 mesh and specifies 100% -20 mesh for its fine potash supplies.

Triple superphosphate must be 100% -10 mesh, with less than 4% moisture content. Although 46% P_2O_5 is most frequently used, 48% material is preferred. Insolubles must be kept below 1% and the free acid (H_3PO_4 basis) content less than 3%.

Ark-Mo purchases all of its liquid raw materials in 8000-gallon tank car quantities, which include anhydrous ammonia (82.35% N_2), nitrogen solutions (37% N_2), and 66° Bé. sulfuric acid. Nitrogen solutions and sulfuric acid are transferred from tank car to storage tanks in about 2 hours with the aid of compressed air (6E). The storage tanks are housed in a frame building, which is kept above 50° F. in the winter with steam heat, to prevent nitrogen solutions from salting out. A 55-hp. boiler furnishes steam for heating and process steam consumed in the ammoniator.

Anhydrous ammonia is removed from tank cars by creating a pressure differential between the cars and the storage vessels. A compressor sucks ammonia vapors from the storage tank and compresses it into the tank car. Process water comes from the city water supply at Walnut Ridge. A check valve in the water line prevents back flow of contaminated water into the main.

Gravimetric feeders control solids

Solid raw materials are removed from storage with a tractor shovel to an elevator equipped with a clod breaker in the intake hopper. Ark-Mo uses four raw material feed hoppers with capacities ranging from 5 to 15 tons. Each hopper is equipped with pneumatic bin unloaders that prevent solids from hanging up. These rubber unloaders are inflated and deflated with air (5E), continuously breaking material away from the sloping sides of the hoppers.

At this point the materials go to either or both of two 10-mesh single deck vibrating screens (15E). Oversize solids are sent to either a chain beater (9E), hammer mill (22E), or both, where they are pulverized and returned to the dry mix elevator (68 feet, 70 tons per hour). (Only one screen and one crusher have been used in actual operation.) Correctly sized material passes on to the ammoniator-granulator (8E).

Table II. Screen Analysis of Potash

Mesh	Potash, %	
	Coarse	Fine
+6	0.0	0.0
6/14	31.5	0.5
14/20	51.1	18.1
20/40	13.5	64.3
40/65	2.7	14.3
-65	1.2	2.8



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A tractor shovel removes solid raw materials from the storage area and delivers them to a bucket (55 feet, 70 tons per hour) elevator equipped with a clod breaker (10E) in the intake hopper. The materials are then transported to a conveyor belt (20 inches \times 34 feet) and carried into a system of chutes above the feed hoppers. Bin level indicator lights and pneumatic valves (4-way butterfly-type) which control flopgates in the chutes enable the tractor operator to properly charge the various hoppers.

Ark-Mo makes its own normal superphosphate (20% P_2O_5) in a unit about 300 yards away from the granulation plant. This material is hauled in 5-ton dump trucks to an elevator at the raw materials building; the elevator unloads onto a suspended pivoted screw conveyor which distributes superphosphate over the storage area. (Superphosphate forms a screw trough for the suspended screw conveyor.)

Triple superphosphate comes in by box car and is unloaded with tractor shovels into a second raw materials elevator. This elevator delivers the raw material to a belt conveyor. From this

point triple superphosphate goes to a second screw conveyor similar to the one which handles normal superphosphate. The raw material is then piled up in a separate part of the storage area.

Potash, also received in box cars, is unloaded with tractor shovels and transported by the same elevator that handles the triple superphosphate. The belt conveyor which receives this material has a flopgate arrangement at the discharge end for directing potash to its proper storage area.

Ark-Mo also has an underground screw conveyor for unloading hopper-bottom cars. This conveyor delivers the raw materials to the elevator used for transporting both potash and triple superphosphate.

Ammonium sulfate, which arrives in box cars, is unloaded with tractor shovels and dumped directly into its storage bin. The same procedure is used for handling inert material employed in some formulations. For its inert material, Ark-Mo uses dolomite stone, which has the advantage of adding calcium and magnesium to their product.



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Ammoniation and granulation in one step

In the ammoniator-granulator, all solid and liquid raw materials are mixed together. Air is blown onto the moving bed of material by a fan (2E) which is driven by a 7.5-hp. motor. A suction fan (2E), driven by a 5-hp. motor, removes steam generated by chemical reactions that take place in the ammoniator.

Material from the ammoniator goes to the dryer and is moved to the cooler (7E) by a vibratory conveyor, 2 feet wide by 8 feet 3 inches long. A 20-hp. motor drives the 7-foot diameter by 30-foot long cooler. Air, flowing countercurrent to the flow of solids, is drawn through the unit by a fan, 1080 r.p.m. (4E) on the cooler dust cyclone (7E). The fan is driven by a 30-hp. motor.

The 15-ton superphosphate hopper has a gravimetric feeder (13E) with a maximum delivery rate of 54,000 pounds per hour. All other raw material hoppers (5- and 10-ton capacity) are equipped with 28,000 pound-per-hour feeders (11E, 12E). These feeders unload on a common belt conveyor (20 inches \times 59 feet) which carries the raw materials to an elevator (68 feet, 70 tons per hour).

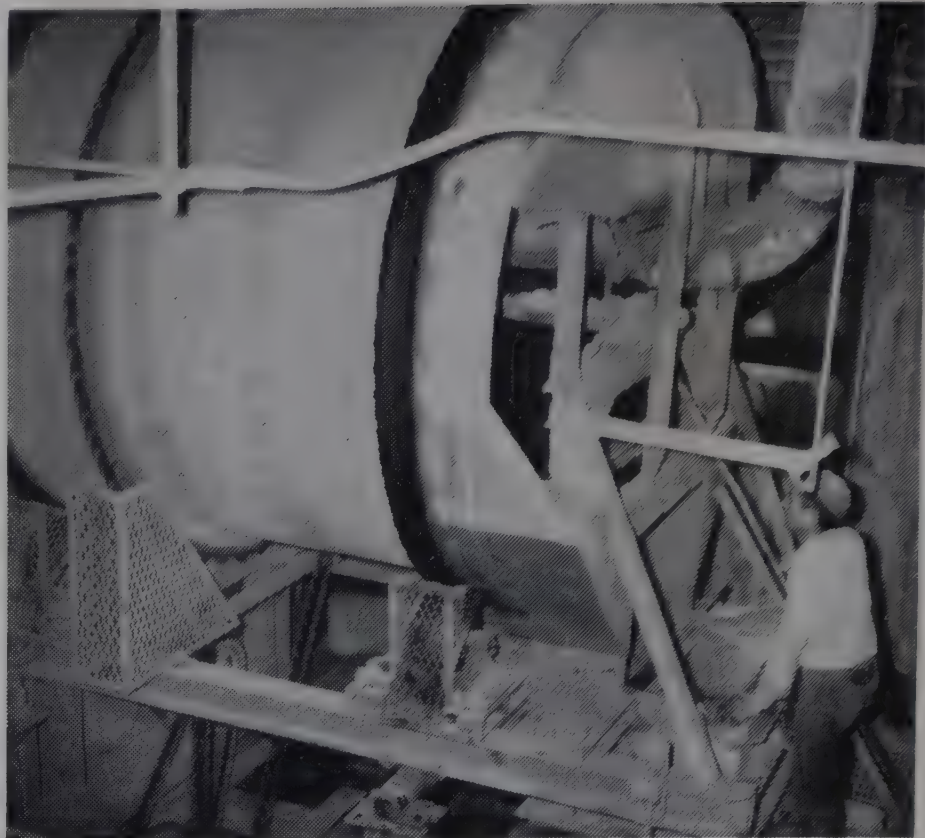


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Nitrogen solutions are pumped (19E) from their storage tanks and metered through a flow meter (4I) in the control room. From here the liquids go into a mixing pipe which introduces them into the ammoniator-granulator (8E). A sparger ensures even distribution of the liquids under the bed of solid materials in the ammoniator.

When anhydrous ammonia is used in some formulations, it is pumped (21E) from its storage vessel, metered through a flow meter (2I) in the control room, and sent to the mixing pipe to be combined with other liquids going to the ammoniator. Water is also metered (1I) into the mixing pipe when needed.

Sulfuric acid, and in some cases phosphoric acid, is also pumped (20E) from storage vessels, and metered (2I) in the control room, but these liquids enter the ammoniator through a separate mixing pipe and sparger. Since steam and sulfuric acid are not used in the same formulations, steam also enters the ammoniator through the acid sparger. A separate flow meter (3I) regulates the flow of steam.



All solid and liquid raw materials are mixed together in the ammoniator-granulator, a cylindrical vessel 7 feet in diameter and 8 feet long, with a 27-inch retarding ring in the center. Ammoniation takes place in the first 4 feet; the remaining 4 feet act as a granulator. A 15-hp. motor drives the ammoniator-granulator through a variable speed drive at a normal rate of 7 r.p.m. The motor is equipped with an ammeter so that overload conditions can be detected whenever large masses begin to form in the ammoniator.



Material from the ammoniator goes to a dryer (8E), 8 feet in diameter and 40 feet long, driven by a 40-hp. motor. Heat is supplied from a 10,000,000 B.t.u. per hour combustion chamber; gases are introduced cocurrent with the flow of solids. The first 3 feet of the dryer has directional flights to move the material forward, but the second 3 feet is empty and serves as a secondary granulator. Lifting flights begin at the 6-foot point and continue to the discharge end. A 40-hp. motor drives an exhaust fan 895 r.p.m. (4E) on the dust cyclone (8E) connected to the dryer.

With easy to granulate materials, humidities must be kept fairly low in the dryer to prevent the product from caking. Higher humidities are maintained with products that are slow granulating, like 5-10-5 grades which contain a filler, so that the dryer acts as an auxiliary granulator.

Product from the cooler discharges into the finished product elevator (60 feet, 70 tons per hour) and is carried up to a double deck vibrating screen (14E). The top screen is 6 mesh, but the bottom screen may be either 14 or 20 mesh, depending on the grade being formulated.

Oversize material from the vibrating screen passes through a chain beater (10E) and is returned to the screen. Fines go into a product recycle storage (25-ton capacity) hopper along with dust from the dryer and cooler cyclones.

After screening, properly sized product dumps onto the finished product conveyor which continuously weighs (1E) the material going to storage. (Storage bins must be tightly enclosed, if made of wood, otherwise the granular material trickles from one bin to another.) The conveyor is also equipped with a tripper so that certain grades of material may be diverted to the parting agent unit (rotating drum).

The 25-ton product recycle hopper—like the superphosphate hopper—has a gravimetric feeding device (13E), with a maximum delivery of 54,000 pounds per hour. This feeder discharges recycle onto the raw materials belt conveyor (20 inches × 59 feet).

Temperatures at various points in the process (Table III) are followed by a thermoindicator (5I) and a 6-point temperature recorder (5I).



Table III. Operating Data

Grade	14-14-14 ^a	14-14-14	12-12-12	10-10-10	16-20-0	10-20-0	3-9-27
Flow Rates							
Process flow rates, tons/hour							
Product output	10	8	8	15	10	10	10
Recycle	21.6	27	24	27.7	21.6	6.8	4.5
Raw material feed rates, lb./hour							
Nitrogen solution	5960	6096	5192	8145	8650	5400	1090
Ammonia, anhydrous	250
Sulfuric acid, 66° Bé.	1330	1552	1192	1800	1360
Potash	4680	3744	3200	4995	9000
Superphosphate, normal	...	1680	5912	15375	6550	13300	9000
Superphosphate, triple	6060	4128	1656	...	6210	2960	...
Filler	1305	1110
Ammonium sulfate	3000
Gas flow rates, C.F.M.							
Natural gas consumption	33.3	35.0	35.8	58.3	61.7	58.3	58.3
Air flow through dryer	16700	14200	13500	13500	15600	14700	10650
Air flow through cooler	15000	15000	15000	15000	15000	15000	4095
Temperatures and Humidities							
Temperatures, ° F.							
Atmospheric	60	62	82	71	57	61	79
Burner air	68	65	85	75	63	64	86
Ammoniator	185	180	175	175	190	160	205
Dryer throat	390	420	402	410	350	...	410
Dryer stack	182	195	190	175	175	180	197
Dryer discharge	180	190	185	170	170	165	200
Cooler stack	140	145	150	140	135	130	150
Cooler discharge	390	...	135	121
Finished product	125	120	120	125	115	85	120
Humidities, (#water/# dry air)							
Atmospheric	0.0095	0.0094	0.0087	0.0095	0.0080	0.0090	0.019
Dryer stack	0.062	0.052	0.035	0.075	0.065	0.048	0.094
Cooler stack	0.035	0.026	0.024	0.037	0.021	0.020	0.024
Humidities, dry bulb temp., ° F.							
Atmospheric	60	62	82	71	57	61	79
Dryer stack	138	175	137	168	169	155	190
Cooler stack	171	140	170	139	139	90	130
Humidities, relative %							
Atmospheric	87	79	44	60	83	81	89
Dryer stack	48	18	29	28	24	26	21
Cooler stack	13	29	9	30	17	66	25

^a Ammonium sulfate, 3 units.

Design changes have been recommended

Inasmuch as Ark-Mo operators have never used both single deck vibrating screens (15E) simultaneously, and have been able to get by with only one raw material crusher instead of two (9E, 22E), changes are suggested in dry mix preparation. Both single deck screens could be replaced by an electric screen, Type 38 (18E). Two cage mills would probably grind the raw materials (especially triple superphosphate) better than the chain beater (9E) and hammer mill (22E) now employed.

For those manufacturers who cannot afford four separate raw material hoppers, it would be possible to mix the materials in a single hopper, at the expense of some operating flexibility. Certain liquid raw materials might be consumed directly from their tank cars, eliminating storage vessels, in localities where adequate supplies and prompt delivery are assured. Small plants could eliminate some liquid raw materials pumps by substituting a pneumatic transport system.

Some 30 different grades of mixed fertilizer have been produced at Walnut Ridge. Operational data (Table III) on the 14-14-14 grade indicates that 27 tons per hour of recycle are needed for a product output of eight tons per hour. (A formulation high in liquids, 1-1-1 ratios containing 30 or more units of plant food, requires considerable recycle to maintain proper plasticity.) Product temperature (Table III) in this case produced a recycle with too much heat content, although the temperature did not go above 140° F., the maximum allowable level for prevention of phosphorus pentoxide reversion. Greater cooling capacity would have reduced considerably the flow of recycle. Ark-Mo officials are now recommending that the cooler (7E) be designed as large as the rotary dryer, 8 × 40 feet (8E).

Product from the cooler exit analyzed 28.4% held on a 6-mesh sieve (Table IV). Much of this material must be broken up in order to meet product size specifications, which causes too many jagged particles in the final mixture. Furthermore, the small particles made from larger particles are not dry enough to ensure proper mechanical condition. Material of +6 mesh could be removed from the dryer, crushed, screened, and returned to the

front end of the dryer. This system would eliminate the need for a double deck screen (14E) after the cooler, but it requires two single deck screens.

Perhaps a better alternative would be to return oversize product from the double deck screen (14E), through the chain beater, 1030 r.p.m. (10E), and then back to the front end of the dryer.

Going to the other extremes of product formulation, the 3-9-27 grade may contain but a small amount of liquids for economical formulation. (A large amount of liquid is added for granulation because it has a low content of highly soluble salts, such as ammonium nitrate or urea.) In this case 4.5 tons per hour of recycle are needed to maintain a product throughput of 10 tons per hour. Recycle is employed only to remove the -20-mesh material from the finished product.

Liquids content in the formulation is low, and recycle actually hinders granulation by competing with other solid materials present. (Steam must be added to this formulation to bring about proper granulation.) Ark-Mo operators say it would be advisable to design a system that would return hot, rather than cold, recycle to the process. They have suggested that hot fines from the double deck screen (14E) be returned to the front of the dryer, short circuiting the path to the recycle storage bin, where cooling takes place. It might be advantageous to have a system for returning hot recycle to the cooler when processing this and other formulations.

Ark-Mo's plant was designed with a roll crusher (16E) following the ammoniator, for grinding moist material whenever masses formed in the ammoniator. Under normal operating conditions the roll crusher is not needed for particle size reduction and it never did perform satisfactorily even though rubber rolls were installed. This equipment is no longer essential to the process.

Screen area on the raw materials screens (15E) is a bottleneck in the process. Any new plant of this capacity should be designed with larger screen areas.

Engineers generally had a tendency to underdesign the drives on elevators at the Walnut Ridge installation. The Ark-Mo plant originally used 7.5-hp. motors but then switched to 10-hp.

Table IV. Product Screen Analysis (Per Cent)

Grade	14-14-14 ^a	14-14-14	12-12-12	10-10-10	16-20-0	10-20-0	3-9-27
Ammoniator exit							
6 mesh	44.5	38.6	30.3	42.1	50.9	29.0	9.1
6/14	21.8	20.2	19.0	20.7	21.5	21.3	61.0
14/20	21.6	19.5	22.4	18.9	14.4	28.8	22.4
20/40	12.1	21.7	28.3	18.3	13.2	19.1	7.1
40/65	1.8	0.4
Cooler exit							
6 mesh	24.3	28.4	37.5	28.5	53.5	14.0	14.8
6/14	25.5	24.3	25.1	22.2	19.8	37.4	60.0
14/20	28.5	22.8	20.6	19.8	14.2	26.5	19.6
20/40	21.7	24.5	16.8	29.5	12.5	19.0	5.6
40/65	3.1	...
Finished product							
6 mesh	2.2	4.7	0.0	1.9	4.3	0.0	1.5
6/14	91.1	87.7	95.5	90.3	90.2	58.6	65.0
14/20	6.7	7.6	4.5	7.8	5.5	32.0	33.0
20/40	9.4	0.5
Recycle							
6 mesh	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6/14	9.7	9.0	6.2	5.7	9.9	1.0	0.0
14/20	52.1	42.1	36.4	33.8	36.8	18.0	21.0
20/40	29.1	36.1	38.5	42.4	36.3	61.0	65.0
40/65	9.1	12.8	14.4	18.1	17.0	20.0	14.0

^a Ammonium sulfate, 3 units.

motors. In some cases even 12-hp. motors would have been best, especially when solids tend to hang up in the elevators. All motors driving elevators or rotating equipment should be connected with ammeters in order to detect overload conditions when solids begin to collect, and should be controlled by limit switches (6I).

More recent units like Stauffer Chemical Co.'s \$900,000 Los Angeles plant (2), are going to a system of interlocking electronic controls for the feeding of solid raw materials from the hoppers to the common conveyor belt. Also, there is a trend in the industry toward greater instrumentation.

Ark-Mo's system for coating the granulated product, in order to prevent the product from caking during storage, had a rotating drum, a dust collecting fan (3E), parting agent storage bin, parting agent feeder (17E), and a product return bucket elevator (45 feet, 70 tons per hour). This system is now inoperative; diatomaceous earth (12) is spread by hand over the product as it moves along the conveyor belt carrying it to storage. New plants could be designed without this system, at a saving of about \$7000.

Even though the Ark-Mo installation represents the latest technology, experts still believe that there is insufficient information on the art of granulation in order to construct an ideal plant. There is need for more information on liquid distribution and depth of bed in the ammoniator, maximum allowable dryer temperature, maximum moisture in the finished product, best parting or coating agents, and many other factors. Until better design data are forthcoming, Ark-Mo operators suggest sparger openings of $\frac{3}{12}$ inch, a thin layer of solids in the ammoniator, dryer throat temperatures of 350° to 500° F., and 2% maximum moisture content in the finished product.

Consumption patterns are shifting

Throughout the industry, nitrogen and potash consumption have increased at a much faster rate than the use of phosphate fertilizers (8). Over the past 10 years, when phosphate usage climbed only 60%, nitrogen consumption tripled, and potash consumption more than doubled. Meanwhile, the ratio of plant nutrients (N to P_2O_5 to K_2O) in mixed fertilizer shifted from about 1:2.5:2 prior to 1945, to a value near 1:2:2 today (Table V). Leaders in the industry say that nitrogen usage in the near future will probably exceed that of the other plant nutrients.

Table V. Ratio of Primary Plant Nutrients in Mixed Fertilizer

Year	N	P_2O_5	K_2O
1920	1	4.00	1.05
1925	1	2.76	1.64
1930	1	3.16	1.61
1935	1	2.67	1.58
1940	1	2.56	1.73
1945	1	2.59	1.90
1950	1	2.71	2.10
1955	1	2.16	1.96

Fertilizer prices have declined considerably, when compared on a basis that accounts for decreased purchasing power of the dollar. Hignett (8) has shown that the current unit price of nitrogen is down to only one third of the adjusted 1920 value. A unit of potash now costs only one fifth as much, and a unit of phosphorus pentoxide only 73% of the 1920 price. Relatively lower prices for nitrogen and potash have probably been an important factor in the increased use of fertilizers. No doubt they have had their effect on the proportions of plant nutrients now marketed, as indicated by the increase in nitrogen consumption.

Even greater changes have taken place in the pattern of raw material utilization, again reflected in the relative price structure.

Prior to 1920, natural organics were the principal sources of nitrogen and generally the cheapest, but they have been on their way out ever since. By-product ammonium sulfate (from coke ovens) was an important source at that time, but nitrate of soda took the lead from 1920 to 1950.

As early as 1930, synthetic ammonia supplied about one third of all the fertilizer nitrogen, a position it held for the next 10 years. At the close of World War II, however, the use of synthetic ammonia soared to a point where this material now supplies about 88% of the fertilizer nitrogen in its various forms (anhydrous ammonia, ammonium nitrate, ammonium sulfate, urea, ammonium phosphates, sodium nitrate, and nitrogen solutions).

The use of anhydrous ammonia and ammoniating solutions for direct application into the ground now account for 22% of the total nitrogen usage, while solid ammonium nitrate supplies 23%. Ammonium sulfate supplies about 18% of the nitrogen requirements, almost equally divided between synthetic and by-product material.

In the past two years, urea consumption has increased sharply. [For example, Ark-Mo is considering the utilization of urea solutions (10) and diammonium phosphate as additional raw materials.] Processes that produce combination fertilizers—ammonium phosphates and nitric phosphates—are also coming to the front.

Technology is changing

The depletion of the soils, and the need for greater farming efficiency (because of acreage allotments), continues to place increased emphasis on the use of high-analysis products. At least three other high-analysis processes, in recent years, have received considerable attention in the industry, and some have been viewed with apprehension by the smaller producer who feels that his competitive position may be jeopardized by technological advances.

Processes using nitric acid alone and in combination with sulfuric acid for acidulating phosphate rock have been used in Europe for many years, particularly in France. The capital investment for this type of plant can run as high as \$4 million—beyond the means of most small fertilizer manufacturers (15). What frightens them most are the numerous claims for raw material savings, some of which are justified. Should sulfur shortages again occur in this country, or if sulfur prices go high enough, large producers will undoubtedly take a closer look at this process.

In the early 1950's, when sulfur shortages stimulated keen interest in nitric phosphate processes, 16 companies were given certificates of necessity to build plants. But interest waned when sulfur again became readily available. Only two plants were actually built, one by Allied Chemical & Dye Corp., South Point, Ohio, and another by Associated Cooperatives, Inc., at Sheffield, Ala. Other companies are considering plants, however, and it seems likely that one or more new units will be built in the near future.

Four nitric phosphate processes have been developed through the pilot plant stage by TVA since 1943 (7, 9, 13, 14, 21). Stanfield (19) has discussed the economics of these processes in comparison with conventional fertilizer production methods. Most of the TVA work was done without knowledge of European progress during World War II, but the methods are similar.

The process, generally speaking, uses multiple vessels for acidulation of phosphate rock with nitric and sulfuric acids in the presence of ammonia. Potassium chloride is added to make a 11-11-11 grade product, and some manufacturers go as high as 14-14-14. If 1-2-1 or 1-3-1 ratios are desired, additional phosphorus pentoxide may be added as triple superphosphate, but this practice somewhat offsets raw material advantages inherent in the process.

Nitric-sulfuric acidulation involves higher investment and

operating costs, and does not have the flexibility of other processes, but this is no real barrier for the larger manufacturer who wishes to take advantage of cheaper raw materials. In any event the process has been proved commercially and is available to those who can afford it.

Nitric acid-carbon dioxide acidulation, another variation of this process, uses carbon dioxide gas instead of sulfuric acid to acidulate phosphate rock. No plants are being installed in this country, although the process is operated commercially in Europe and has been studied by a number of American companies.

Production costs are reported to be less than those of the nitric-sulfuric acidulation process (15), and the operation has similar limitations regarding flexibility and capital investment. In addition, it must be located near a cheap source of carbon dioxide. Sulfate radical in this case is added by small amounts of magnesium sulfate which is supposed to improve granular form of the product.

In recent months TVA engineers have worked out a continuous process for production of a highly concentrated nitrogen-phosphate fertilizer from ammonia and phosphorus pentoxide (20). They produced, in pilot plant operations, a granular material containing 17% nitrogen and 73% phosphorus pentoxide. The product is predominantly ammonium metaphosphate and a mixture of complex nitrogen-phosphorus compounds. Potash was added during the hydrolysis step in some tests to make nitrogen-phosphorus pentoxide-potassium oxide fertilizers.

Combination fertilizer processes based on ammonium phosphate—currently employed in this country and in Canada—are being offered for sale by at least two engineering companies. They are essentially a three-step operation. Phosphate rock is acidulated with sulfuric acid and calcium sulfate is filtered off leaving only phosphoric acid. The wet-process acid is then reacted with ammonia to produce impure monoammonium phosphate, diammonium phosphate, or mixtures of these salts. Required formulations are made up by the addition of more sulfuric acid and ammonia, together with potassium chloride, prior to granulation.

Another variation of this process could be developed, although it has not been proved by any commercial operations. It is technically feasible to supply the additional nitrogen with nitrogen solutions instead of ammonia and sulfuric acid, in order to make up high-nitrogen formulations.

TVA engineers have produced ammonium phosphate-nitrates in their ammoniator on a pilot plant scale. (Potash may be added if desired.) They have manufactured such grades as 16-48-0, 11-22-22, and 16-22-16, and are continuing their development work.

In spite of major technological advances, the conventional mixing process that uses ammonium sulfate as the major source of nitrogen, and the technique of ammoniating triple superphosphate, can both be highly competitive with other operations. For the smaller producer they are more desirable from the standpoint of capital investment. Inasmuch as the industry itself has more small plants than large ones, continued activity and interest in these two processes is anticipated for the immediate future.

Acknowledgment

The authors are grateful to Earl Rash of Ark-Mo Plant Food Co. for his contributed information on operating know-how. Acknowledgment is made, also, of the technical contributions by M. A. Tschantre and the TVA staff, and J. C. Sharp of Spencer Chemical Co.

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- (7E) General American Transportation Corp., Chicago 90, Ill., rotary cooler, 7 by 30 feet; cyclone dust collector, No. 24.
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Granulated Triple Superphosphate

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in collaboration with

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EARLY in 1954, Davison Chemical Co. (now a division of W. R. Grace), put into operation near Bartow, Fla., a modern triple superphosphate plant with an annual designed capacity of 200,000 tons. The plant was completely designed and engineered by the Dorr Co. (now Dorr-Oliver). The Dorrco Granulated Triple Process which is employed is unique in this country in that it yields, directly, in continuous operation a granulated triple superphosphate.

Triple superphosphate is a highly concentrated phosphate fertilizer containing 43 to 48% available phosphorus pentoxide, P_2O_5 . In 1930, production in this country from five plants amounted to only 100,000 tons; by 1952, 13 plants were in operation producing over 862,000 tons. In 1955, U. S. production exceeded 1,500,000 tons. Production rates over the last 13 years are shown. During the same period, production of normal superphosphate has increased to high levels but not at the accelerated rate shown by triple superphosphate.

The manufacture of ordinary super-

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phosphate (7) is obviously not as complicated or costly as production of triple. An integrated triple superphosphate plant entails a greater capital investment—the Davison plant cost \$10,400,000. Additional labor and processing make unit phosphorus pentoxide costs higher than in ordinary superphosphate. But triple has the advantage “on the long haul.” With increasing transportation costs, demand for the concentrated fertilizer products has kept pace in spite of the higher price. Another important factor in the rapid growth of triple is that lower grades of phosphate rock (cheaper than that required for ordinary superphosphate) may be used in its manufacture.

To produce normal superphosphate, ground phosphate rock is mixed with the proper proportions of sulfuric acid; the resultant mass is allowed to set up and is finally cured in large storage piles. To produce triple superphosphate, phosphoric instead of sulfuric acid is used to decompose the phosphate rock.

Triple superphosphate is being made from both electric furnace phosphoric acid and wet process phosphoric acid.

Furnace acid is highly concentrated and almost free from contaminants. Wet process phosphoric acid, on the other hand, while generally cheaper is relatively dilute and contains substantial amounts of impurities. Waggaman (12) has compared the number of steps involved in making superphosphate and in making triple superphosphate by sulfuric acid and by electric processes.

The reactions between phosphate rock and the higher concentrations of furnace grade phosphoric acid have been studied extensively by Tennessee Valley Authority workers (2, 3). Pilot units and semicommercial plants have been built by the TVA. Initially batch processes were used but later continuous processes were evolved (3). Big advantage in using furnace acid is elimination of the evaporation step required with more dilute wet process acid. In the last analysis, the economics determine which type acid should be used by a given company in a specific location.

In a special chapter (12), W. C. Weber describes the manufacture of phosphoric acid by the wet process. The unit making strong phosphoric acid at Consolidated Mining & Smelting Co.'s

plant in Trail, British Columbia, Can., has been described by both Weber (14, 16) and Atwell (1).

The history of triple superphosphate manufacture dating from 1872 when it was first made in Germany has been outlined by Porter and Frisken (11). These authors described the Immingham (England) plant of Fisons, Ltd. The Fisons plant, designed and engineered by Dorr, uses a process similar to that used by Davison in its Bartow plant. Capacity of the British plant, however, is only 230 tons of product per day.

Triple superphosphate production in the United States began in 1890 or 1891. American Phosphate and Chemical Co., Baltimore, was the first to make triple in this country. Goulding Fertilizer built a plant in Pensacola, Fla., in 1898. Virginia-Carolina Chemical built its Charleston, S. C., plant, which is still operating, in 1907.

Piedmont Electro Chemical Co., Mount Holly, N. C., made the first attempt to use electric furnace phosphoric acid in the process. The plant started operation in 1914 but was aban-

doned in 1916 when it became apparent that anticipated cheap electric power would not materialize.

Large Deposits of Phosphate Rock in Florida. Florida is a logical location for a triple superphosphate plant. More than one third of the world's annual production of phosphate rock comes from the pebble deposits of central Florida. It is found in an unconsolidated matrix of pebble phosphate, clay, and sand, called the Bone Valley formation. The rock, fossilized bones of marine creatures, was deposited millions of years ago by ancient seas that covered the land.

Florida's pebble phosphate is recovered by open-pit mining methods. Currently eight companies are mining phosphate in the central Florida area. They are:

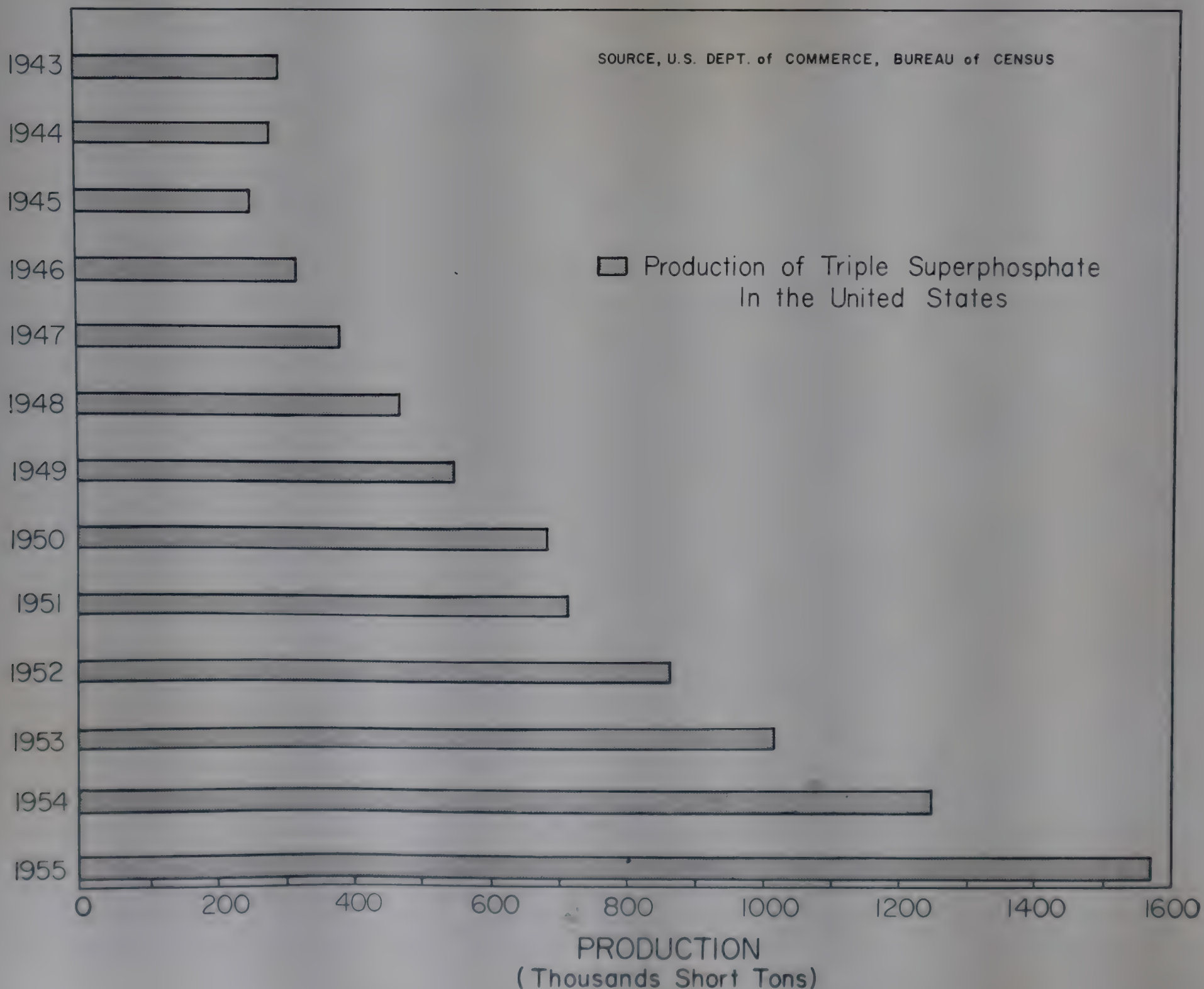
American Agricultural Chemical Co.
American Cyanamid Corp.
Armour & Co.
Coronet Phosphate Co., Div. of Smith-Douglas
Davison Chemical Co., Div. of W. R. Grace

International Minerals & Chemical Corp.
Swift & Co.
Virginia-Carolina Chemical Co.

Several of these firms produce triple superphosphate. Other firms producing triple have located plants near the Tennessee or western phosphate deposits or near consuming areas.

Large draglines are used to remove the overburden which varies in thickness from 2 to 60 feet. The earth is dumped onto adjacent ground, or, more generally, used as fill in previously mined areas. The matrix, also removed by dragline, is dumped into a well or shallow pit next to the mining cut. Here it is whipped into a thick slurry by hydraulic guns supplied with high pressure water. The slurry is then pumped by dredge pumps to a nearby washer and recovery plant.

At the recovery plant the matrix is washed, sand removed, and slimes discarded. Clear wash water is recirculated to the hydraulic guns. Phosphate pebbles (seldom larger than 1 inch in diameter) are screened out. Finer par-



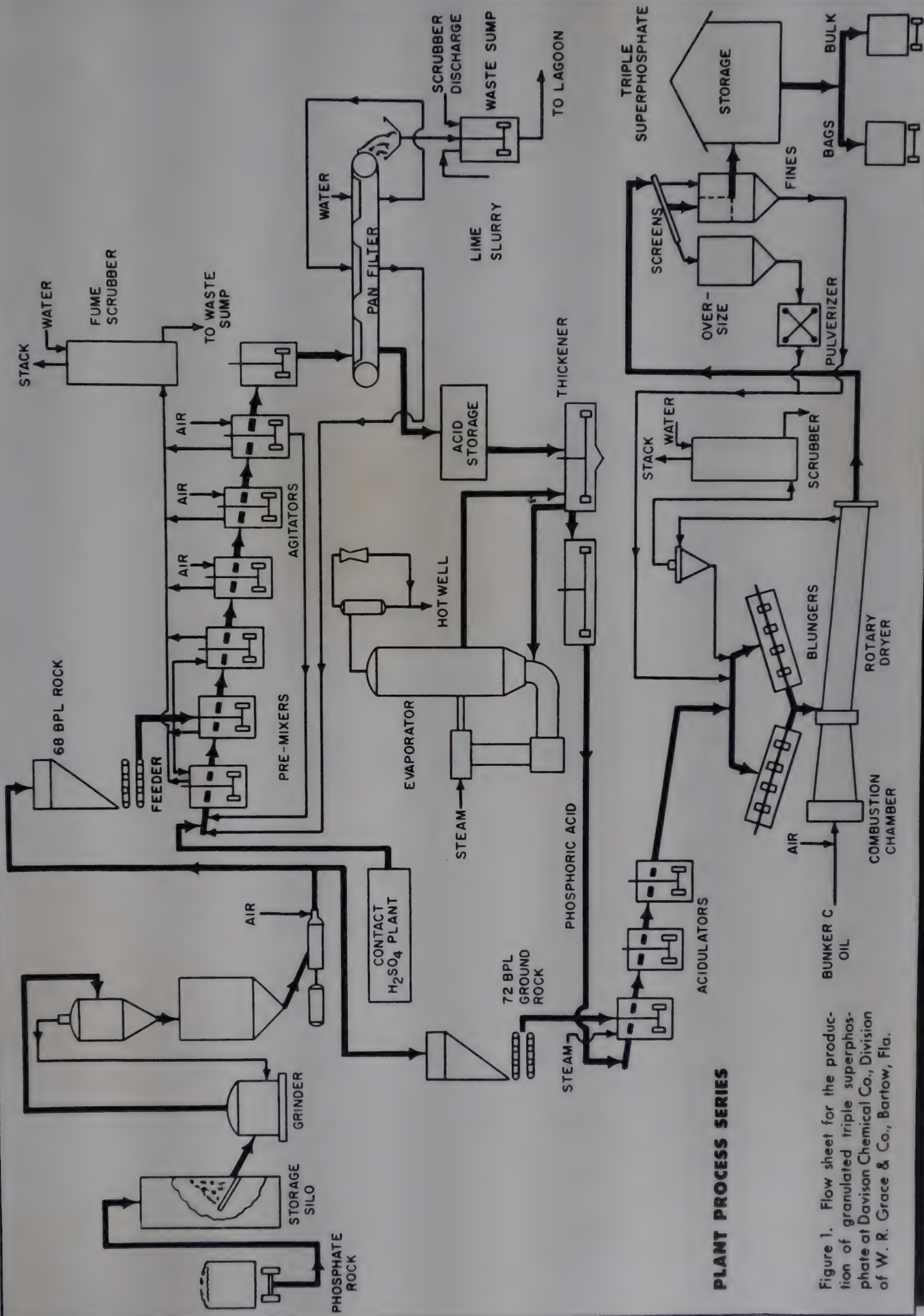


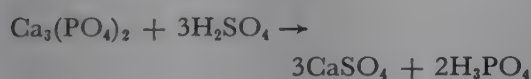
Figure 1. Flow sheet for the production of granulated triple superphosphate at Davison Chemical Co., Division of W. R. Grace & Co., Bartow, Fla.

ticles of phosphate are recovered by flotation or the table agglomeration processes.

Chemistry of the Process

Florida phosphate rock is a noncrystalline amorphous phosphorite consisting principally of fluorapatite—a compound of tricalcium phosphate and calcium fluoride. In addition, nearly all phosphate rock contains many impurities including organic matter, iron and aluminum oxides, carbonates of lime and magnesium, and small quantities of sodium, potassium, chromium, vanadium, and uranium.

The principal reaction occurring in the phosphoric acid unit is the reaction between tricalcium phosphate and sulfuric acid to give phosphoric acid and insoluble calcium sulfate (13):

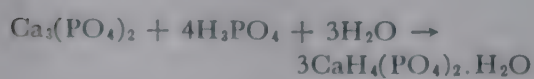


In addition various side reactions take place—for example, the reaction between calcium fluoride, sulfuric acid, and water to give gypsum and hydrofluoric acid; also the reaction between hydrofluoric acid and silica to give hydrofluosilicic acid and water.

Chemistry involved in the phosphoric acid process is relatively simple; it is complicated only by the complex nature of phosphate rock and the extremely corrosive properties of the solutions produced. However, the physical chemistry involved in the production of the optimum type and size of gypsum crystals and the maximum conversion of phosphorous to phosphoric acid is very complicated. Successful operation of the phosphoric acid plant is based on making good gypsum crystals. This in turn depends on the proper and close control of the reaction, particularly reaction temperature and time, dilution, and amount of excess sulfuric acid.

The best filtration characteristics are obtained from rather large individual rhombic gypsum crystals of a shape wherein the length does not exceed two or three times the width. In plant operation, microscopic examination of the gypsum is made on a regular basis to determine the type of crystals being formed.

Phosphoric Acid and Rock React. The principal reaction occurring in the triple superphosphate section of the plant involves the phosphate rock or tricalcium phosphate, and phosphoric acid to produce monocalcium phosphate:

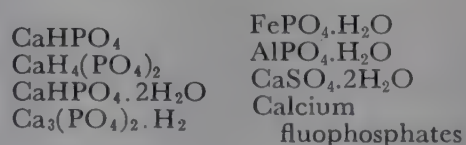


In addition to the desired end product, monocalcium phosphate monohydrate,

Comparison of steps involved in manufacture of ordinary superphosphate and triple superphosphate

Various Steps Involved	Ordinary Super-phosphate	Triple Superphosphate		
		Sulfuric acid process	Electric furnace process	Dorr granular process
Manufacture of elemental phosphorus			✓	
Manufacture of phosphoric acid		✓	✓	✓
Removal of gypsum		✓		✓
Concentration of acid		✓		✓
Mixing of acid and rock	✓	✓	✓	✓
Drying the product				✓
Final curing	✓	✓	✓	
Crushing and screening	✓	✓	✓	

several other compounds can be produced in this reaction. These include:



Acid temperatures and strength in the reactors and product temperature in the driers are closely controlled to avoid formation of undesirable end products.

The primary objective in the reaction tanks is to convert most of the rock tricalcium phosphate to monocalcium phosphate and the remainder to dicalcium phosphate. Dicalcium phosphate converts readily to monocalcium phosphate in the driers where higher temperatures and acid strengths favor this reaction. As in the case of phosphoric acid production, proper control of the reaction is extremely important (8).

The principal features of the Dorco process for the continuous production of granular triple superphosphate are the use of a relatively dilute (39% P_2O_5) phosphoric acid which produces a fluid reaction slurry, and the recirculation of a very large proportion of the dried product for mixing with the reaction slurry. Approximately 10 to 20 tons of finished

material are recycled to the mixing or blunging station for each ton of product.

Theoretically therefore, the average product circulates through the system 10 to 20 times before being screened out and sent to production. The product granule is built up in layers. When examined under a magnifying glass a cross section gives an onionlike appearance.

Production at Bartow, Fla.

Davison's triple superphosphate plant, including a contact sulfuric acid unit is located in the heart of the Florida phosphate mining area, near Bartow. The triple plant and rock preparation facilities are connected by rail and served by a plant locomotive. Inbound and outbound freight is handled by the Atlantic Coast Line Railroad.

The process flow sheet, Figure 1, shows how production is divided into two general operations—first, production of phosphoric acid; and second, reaction of phosphoric acid and rock to yield the triple superphosphate.

Pebble Phosphate Rock Received by Rail. Pebble phosphate rock from nearby Davison mines and processing unit is delivered to the plant site in 70-ton ce-



This plant produces lime for neutralization of waste effluent

Waste Disposal

The principal waste products from the plant are gypsum filter cake from the phosphoric acid unit and fume scrubbing tower fluosilicic effluent. The gypsum is collected in a concrete waste sump tank equipped with an agitator. There it is combined with plant waste water and discharge liquors from fume scrubbers. Each section of the plant has fume scrubbers designed for maximum knockdown of fluorides that would otherwise be discharged to the atmosphere.

The contents of the waste sump tank are continuously neutralized by addition of slaked lime slurry. The neutralized waste slurry is pumped through a head box to the waste launder. This is an open 21 × 23 inch wooden trough discharging by gravity into the waste disposal area.

The waste disposal area is a 93-acre artificial lagoon formed in an adjacent mined out area. With this ultimate use in view the mining was done in such a fashion that windrows of overburden were thrown up to create a baffling effect as the effluent flowed through the lagoon and out into the discharge stream. This baffling effect allows sufficient retention time to settle out the gypsum. The effluent is crystal clear.

The pH of the effluent is continuously monitored as it leaves the waste launder. Sufficient lime is added to keep the pH at approximately 6. The lagoon effluent is also monitored on a 24-hour basis to prevent any stream pollution.

Special facilities are provided for unloading, storage and slaking of lime for the neutralization of the plant waste effluent. Pebble lime is received in covered hopper bottomed cars and emptied into a lime track hopper from which it is conveyed and elevated into the lime storage bin for slaking as required.

ment hopper cars and dumped into a track hopper. A reciprocating feeder regulates the flow at 250 tons per hour to an underground rock conveyor (6E) which discharges into the bottom of a bucket elevator (10E). Another conveyor receives rock from the elevator and distributes it by tripper to openings in three storage silos.

The storage silos are of concrete construction each 30 feet in diameter by 47 feet high and holding 1100 tons each. The primary rock (68 bone phosphate of lime, B.P.L.) used for making the phosphoric acid is stored in the outer silos. Secondary rock (72 B.P.L.) used for producing the triple superphosphate is stored in the center silo.

The silos are constructed with an inclined shelf in the upper section with overflow into a dead storage section below. Rock from the "live" storage gravitates through a 12 × 12 inch chute to Raymond grinding mills. Rock from the "dead" storage section of the three silos can be discharged through bin chutes onto a retrieving conveyor which delivers the rock to an elevator and hence, by way of a distributing conveyor back into the live storage section of the proper silo.

The grinding system consists of three Raymond roller mills in separate closed circuits with "whizzer" separators (3E). Piping is such that there is flexibility as to which silo may be used as feed for a given grinder. Rock ground to the desired fineness (about 50%, + 200 mesh for primary rock and under 25%, + 200 mesh for secondary) is carried out of the mill through a 32-inch duct to a cyclone dust collector.

The dust collector discharges by gravity through a dust valve into a cone bottom carbon steel storage bin. There are three of these each holding 120 tons of ground rock.

Rock dust leaving the storage bins is carried by air slides (8E) into a Fuller-Kinyon dust conveying system (9E). The Fuller-Kinyon system is basically a pneumatic conveying system incorporating a screw feed or "pump" and an air blast from multiple nozzles. Design capacity of the dust conveying system is 45 to 50 tons per hour.

Dust may be sent (through 6-inch transfer lines) to either the phosphoric acid or the triple superphosphate section of the plant. A two-way manually operated valve diverts the dust to the proper section. Motor operated valves divert the dust flow to the desired storage bin. Except for the one manually operated valve, the entire Fuller-Kinyon system is operated from a central graphic control board. Lights on the control board indicate lines in use and extent to which each bin is filled.

Phosphate Rock Reacts with Sulfuric Acid. Phosphoric acid production is based on the reaction between 68 B.P.L.

rock with 93% sulfuric acid. At the Bartow plant the equipment is arranged in two trains, each of which may be operated and controlled independently of the other. This arrangement allows continuity of operations even though major shutdowns may be required. However, certain equipment is common to both trains.

Ground phosphate rock discharged from the Fuller-Kinyon system is stored in two dust storage bins. The bins are constructed with two straight and two inclined sides to assist gravity flow.

Rock dust is withdrawn from the bin at a uniform and measured rate by a gravimetric feeder (14E). The feed rate may be varied from 8 to 17 tons per hour.

The weighed phosphate rock is discharged by gravity into one of three pre-mixers. The pre-mixers are 4500-gallon rubber-lined tanks. They are equipped with turbine type agitators driven by 30-hp. motors. Gypsum crystal growth determines the selection of pre-mixer to which the rock is fed. Variations in rock composition, excess sulfuric, temperature operating rate, and equipment availability (maintenance requirements) are the principal reasons for changes in gypsum crystal structure. Rock entry points are changed to alleviate "out of control" conditions and bring crystal growth back in line.

Davison produces its own sulfuric acid in a Monsanto type contact plant adjacent to the triple superphosphate plant. It is of the same general design as a sulfuric acid plant described in an earlier report in this series (9). When it went on stream it was the largest single unit contact plant in the world (4). Rated capacity is 550 tons per day of 100% sulfuric acid.

Acid at 66° Bé. is pumped from storage tanks in the acid area directly to the phosphoric acid building. The acid passes through a flow-recording controller (7E). For a normal rock feed rate of 340 tons per day per train, approximately 26 gallons per minute of sulfuric acid are required.

In the mixing heads the sulfuric acid is combined with "return" acid. Return acid is filtrate resulting from washing of gypsum in a subsequent step. It contains approximately 18 to 20% phosphorous pentoxide. Normally, return acid flow rate is approximately 93 gallons per minute, controlled manually by rotameter settings. The return acid is pumped from rubber-lined receivers at the filters through 4-inch saran-lined piping. The phosphoric acid (return acid) also goes to a splitter box with a 50:50 division to the two acid mixing heads. The mixing heads discharge



Utilities

Sulfuric Acid Plant,
left

Water supply tank
right

Steam. A waste heat boiler in the contact sulfuric acid plant provides steam for the entire plant at 100 pounds per square inch gage. There is also a standby boiler for use in starting up the sulfuric acid plant or for emergency uses. There are a number of steam driven pumps and blowers throughout the plant. Low pressure steam extracted from the turbine drives is used in various process applications.

Electricity. Electric power is bought from public utilities suppliers at a nominal 66,000 volts. Three power transformers each rated at 2,000 kv.-amp. and located in an outdoor substation step down the voltage to 2400 volts. The 2400-volt power is brought into the various buildings to distribution centers which feed the 2400-volt motors and to indoor substations which step down the voltage to 440. To minimize shutdowns caused by insulator arc-overs, the substation insulators are regularly washed by permanently installed high pressure water sprays.

Compressed Air. Two compressors (16E) each with a capacity of 92 cubic feet per minute at 100 pounds per square inch gage provide compressed air for general service throughout the plant. The compressors are complete with standard accessories such as after coolers and air inlet filters. A 57-cubic foot air receiver is also provided. The air compression equipment is located in the phosphoric acid section of the plant and air is piped from there to various instruments and other equipment requiring it.

Water. Three wells provide process water for the entire plant. Water from the deep wells is delivered by two 3000-gallon-per-minute pumps. An elevated water tank holds a supply of 50,000 gallons. A hydropneumatic water storage tank holding 7500 gallons is provided to supply domestic water mains with water at 50 to 55 pounds per square inch gage.



Fume and drier gas scrubbing towers

Fume and Dust Control

The production of phosphoric acid and triple superphosphate carries with it the tremendous problem of adequate fume and dust control. For example, gases are liberated on dilution of sulfuric acid with phosphoric acid. Dust formation from rock grinding and product pulverization is, of course, obvious.

Large steel rubber-lined ducts are provided for removing the fumes and cooling air from the various agitators. Branches lead to the top of each reaction vessel. The header ducts discharge through the bottom of one of the two scrubbing towers.

Each scrubbing tower is 13 feet in diameter and 55 feet high. The towers are rubber-lined and provided with multiple water spray nozzles.

Two rubber-covered fans exhaust the fumes through the header duct and scrubbing tower and discharge them through a spray eliminator and then through a stack to the atmosphere.

The gases liberated in the reactors also contain silicon tetrafluoride which in the presence of water reacts to form soluble hydrofluosilicic acid. Silica is precipitated. Water sprays have been provided inside the fume duct to supply the moisture necessary for this reaction and to wash the sand away.

Two other scrubbing towers, each 20 feet in diameter and 60 feet high, are provided to handle gases and dust from the triple superphosphate section. These towers are also steel rubber-lined with acid-proof brick in the bottom. They are equipped with multiple water spray nozzles.

Water discharged from all of the scrubbing tower flows to the waste sump tank where it is used for repulping the gypsum.

Throughout the grinding and dust transfer system adequate cyclones have been installed. While the plant is not "hospital clean" the operating areas are relatively free of accumulated dust. Cyclones and scrubbing towers have been designed with sufficient capacity to do an efficient cleanup job even when plant is operating in excess of rated capacity.

into the feed launders of the premixers.

The phosphate rock-sulfuric acid reaction takes place in a series of six tanks on each line. The first three are the premixers. Following the three premixers are three 20,000-gallon rubber-lined tanks, each equipped with turbine type agitators. The latter three tanks are referred to as the agitators. The six tanks are mounted on an incline in such a manner that gravity flow (through launders) may be maintained from the first premixer to the last agitator.

A very large volume of the slurry is recirculated through 10-inch rubber-lined piping from the third agitator back to the first premixer. A large recirculation rate is an essential part of the process. When operating at design capacity as much as 2350 gallons per minute may be pumped (15E) back to the first premixer.

A fourth agitator of similar size and construction serves as a surge tank for feeding the filters in a subsequent step. The train of reaction tanks is set up so that any one tank may be cut out of the system by proper placement of slide gates in the launders.

The reaction between phosphate rock and sulfuric acid is exothermic. To maintain the reaction at the optimum temperature of 70° to 75° C., excess heat is removed by blowing a large quantity of low pressure air through the slurry in each reaction tank. Air enters each agitator through a specially designed distributor, which is a horseshoe shaped open bottomed box, with a serrated edge. The lower edge is submerged in the slurry and the bubbles formed carry away excess heat as evaporated water. The air distributors are connected to three cooling fans (2E).

Continuous Filtration. Slurry from the last agitator is pumped to any or all of five Dorr-Oliver traveling pan vacuum filters (4E). These filters are continuous vacuum units using polyethylene filter cloths. This type of filter and its particular application in the Davison plant recently was described in detail (5).

Although five filters are available, under normal operations, only three or four filters are required. The slurry is taken off the header through sections of rubber hose; any combination of the five filters may be used. At capacity a flow of some 246 gallons per minute is divided between the operating filters.

The filter cake, which consists primarily of gypsum, is washed first with weak phosphoric acid and then with hot water. Filtrate from the first section is the strong phosphoric acid (32% P_2O_5); from the first wash comes the return acid which goes back to the reaction train; from the second wash comes a third filtrate which is used for the first wash.

The pans are maintained under continuous vacuum as they traverse the upper deck of the filter. Vacuum is held at 12 to 16 inches of mercury by vacuum pumps (13E).

The filter cake discharged from the end of the traveling pan filter falls by gravity into a launder where it is repulped and flows into the waste sump tank; there it mixes with water from the scrubbing towers and with other water waste from the plant. Under normal conditions as much as 1300 tons of gypsum may be formed per day. The waste sump tank is of concrete construction and is lined with brick and asphalt. It is 16 feet square and 10 feet deep; it is equipped with an agitator for thorough mixing of lime slurry with the acidic wastes.

Evaporators Concentrate Acid. The phosphoric acid filtrate contains approximately 32% phosphorus pentoxide. Three Swenson single effect vacuum evaporators, each 15 feet high and 6.5 feet in diameter are used to concentrate acid to 39% phosphorus pentoxide. Flash chambers are lined with rubber

and heat exchanger tubes are Karbate. Normal operations require only two evaporators. Davison's evaporation system makes use of the Weber recirculation process (17). This involves concentrating a portion of the acid to higher than desired final strength—allowing maximum precipitation of solids in the thickener and minimum tube fouling.

The 32% P_2O_5 acid is pumped from a 15,000-gallon storage tank equipped with a thickener mechanism through a weir box to a thickener (5E). The thickener serves as a feed tank for the evaporators and also as a tank for mixing the evaporator discharge at 41% phosphorus pentoxide with the 32% feed acid. Solids are precipitated and removed in the underflow of the thickeners by sludge pumps and the sludge is returned to the reaction system. The resultant concentration of the acid in the thickener is maintained at 39%. Use of the thickener with recirculated evaporator discharge minimizes solids deposition in the evaporator heat bodies.

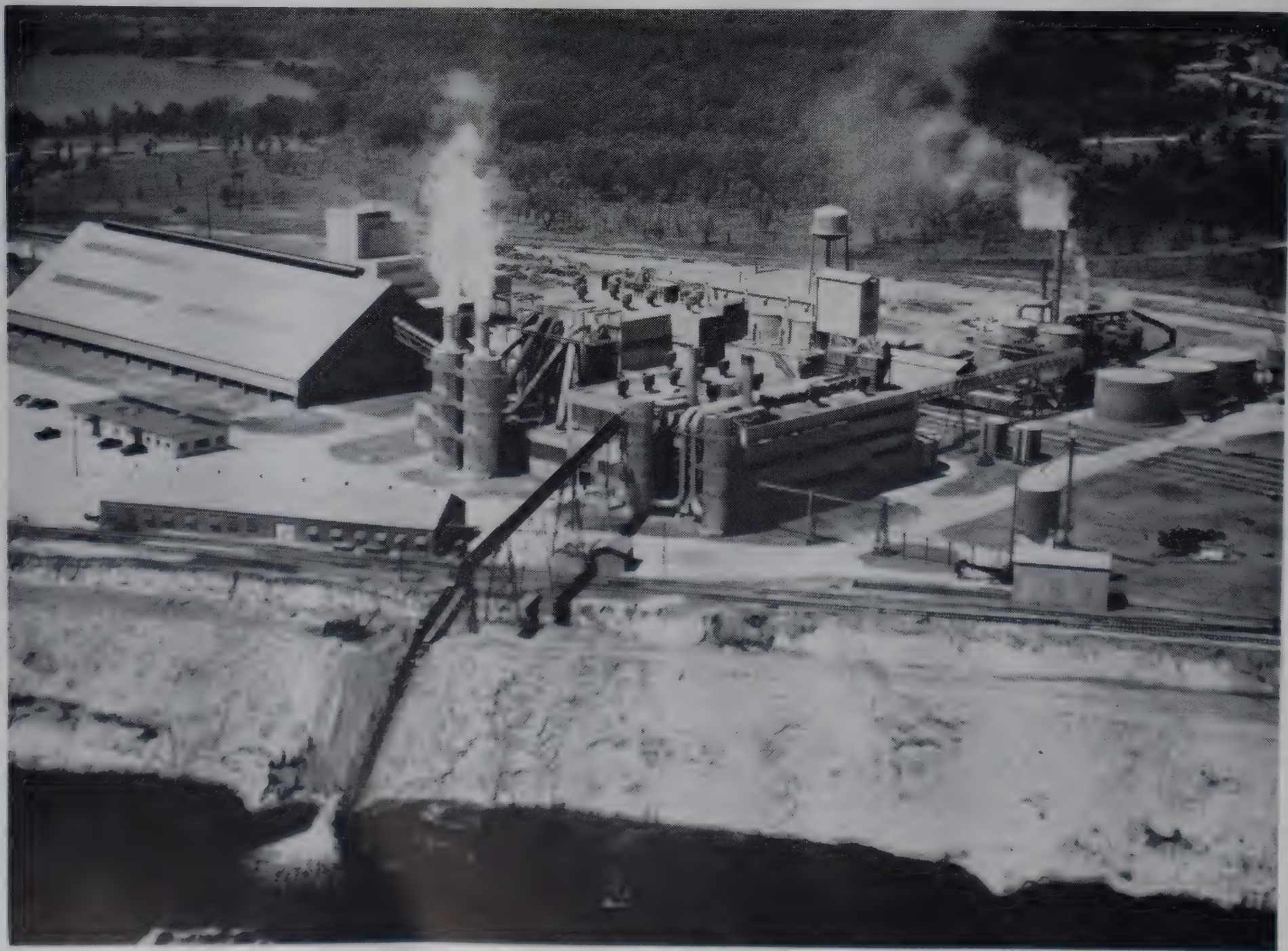
Vapors from the evaporation flash chambers go to condensers discharging

into hot wells. A two-stage steam jet ejector activated by steam at 100 pounds per square inch gage, with intercondenser completes the vacuum equipment. Pressure in the evaporator is controlled at about 3.5 inches of mercury absolute. Phosphorus pentoxide loss is extremely low in this type of concentrating system.

Phosphate Rock and Phosphoric Acid React. The evaporated acid at 39% phosphorus pentoxide is transferred to another storage and thickener tank from which sludge may be pumped. The acid is then pumped to the triple superphosphate unit which, like the phosphoric acid unit, is set up in two parallel trains. In each train the phosphoric acid and 72 B.P.L. phosphate rock react to form the triple superphosphate.

Rock dust is withdrawn from storage bins and measured gravimetrically (14E) into the acidulating tanks. Flow rate may vary from 4 to 8 tons per hour.

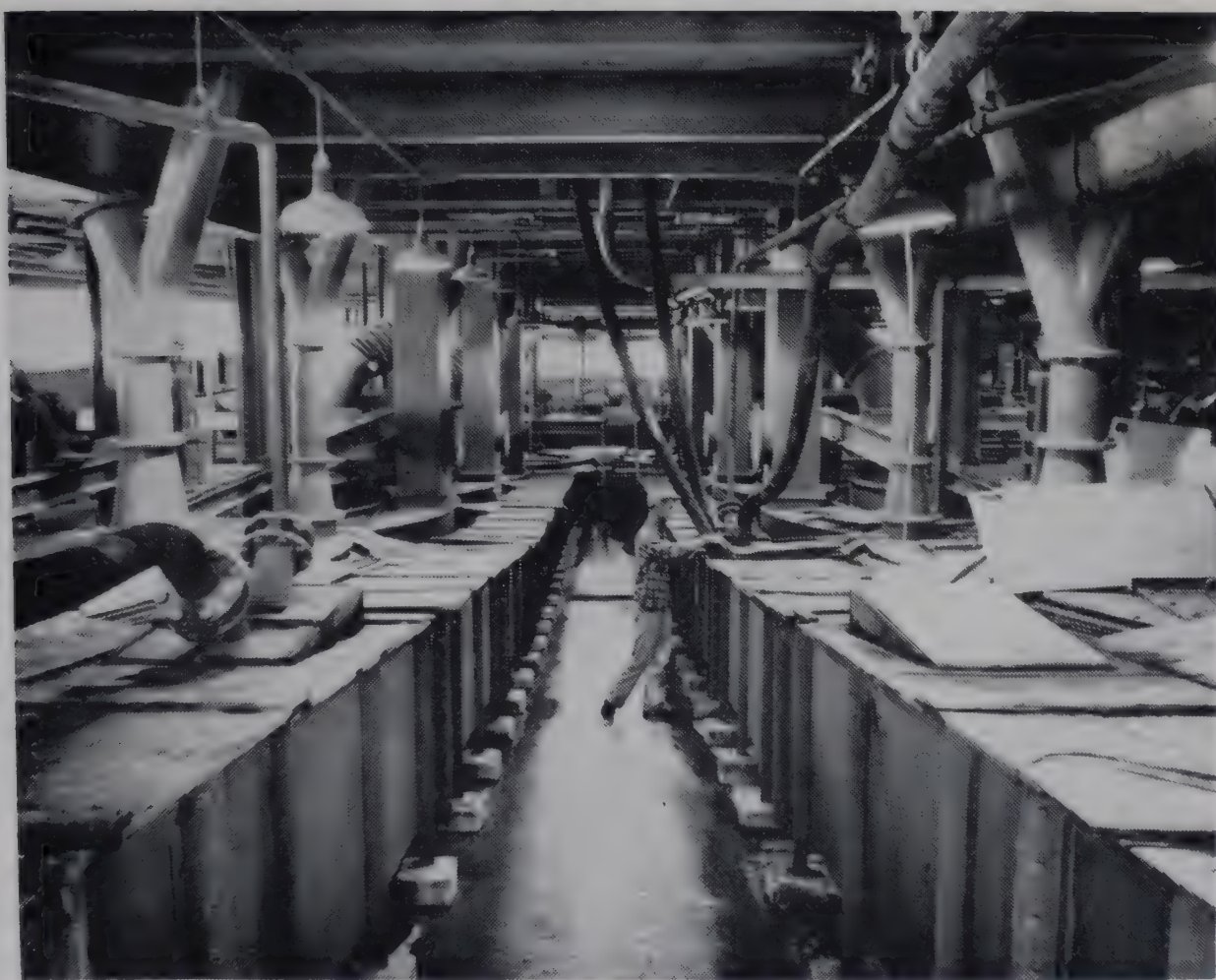
There are three acidulating tanks in each train. These are 3000-gallon lead and brick tanks provided with agitation. The tanks are positioned on an incline



Triple superphosphate plant



Premixers in phosphoric acid section. Rubber-lined recirculation pipes, right background. Cooling ducts, left background



Phosphoric acid section; reaction train launders

so that gravity flow through launders may be used from tank to tank.

The evaporated 39% acid is pumped through a Howard acid type feeder into the first of the acidulators. The feeder consists of four revolving scoops which pick up a measured amount of acid from a constant level compartment and discharge it to the first reaction vessel. Speed of rotation determines flow rate. The acid flow rate is adjusted as a function of the phosphorus pentoxide-calcium oxide ratio in the product—normally 2.26 to 2.30 to 1. This amounts

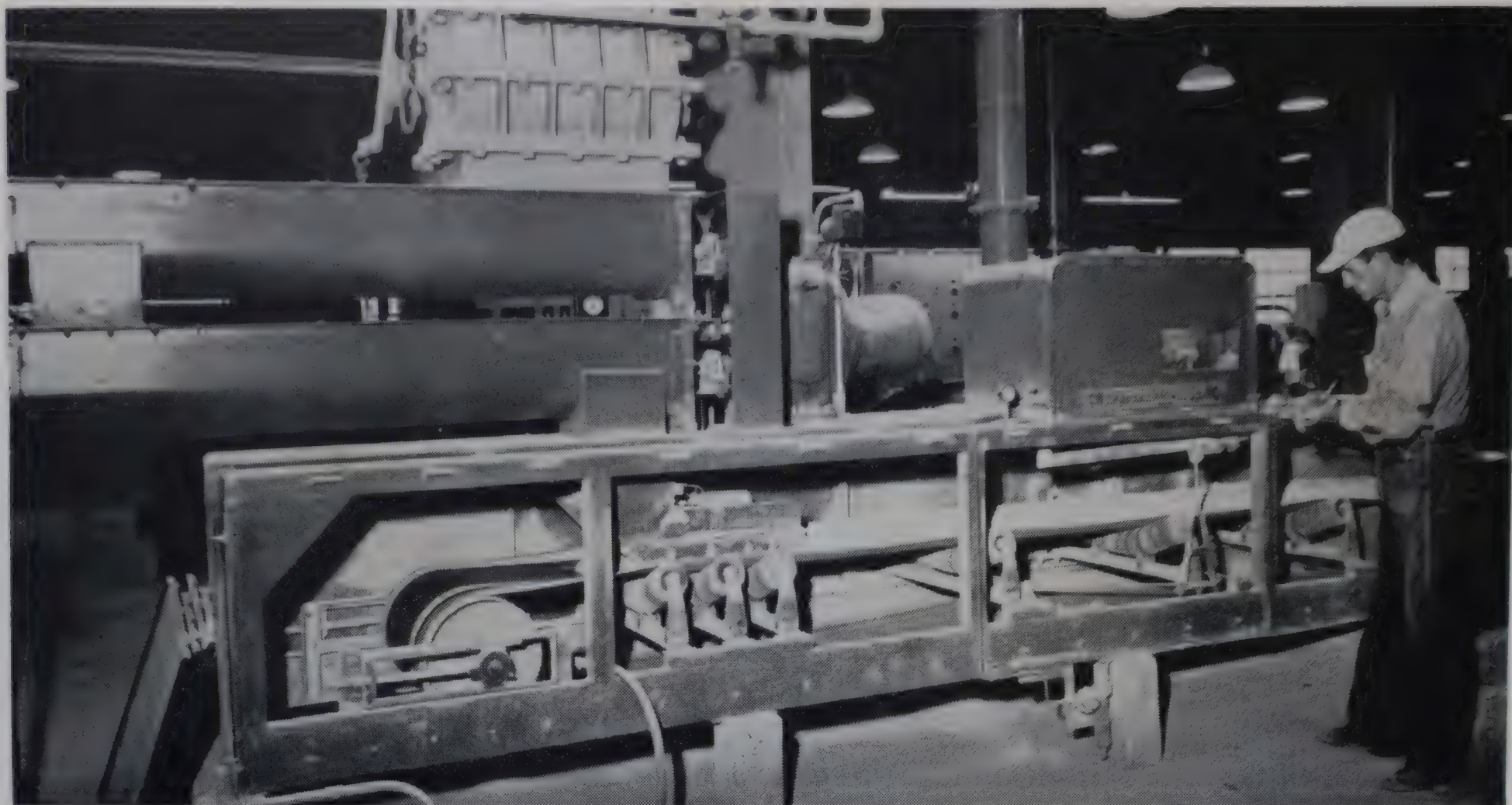
to approximately 29 gallons per minute.

The reaction is exothermic but temperature in the acidulator is controlled by introduction of live steam and varied from 80° to 100° C. depending upon the concentration of the feed acid.

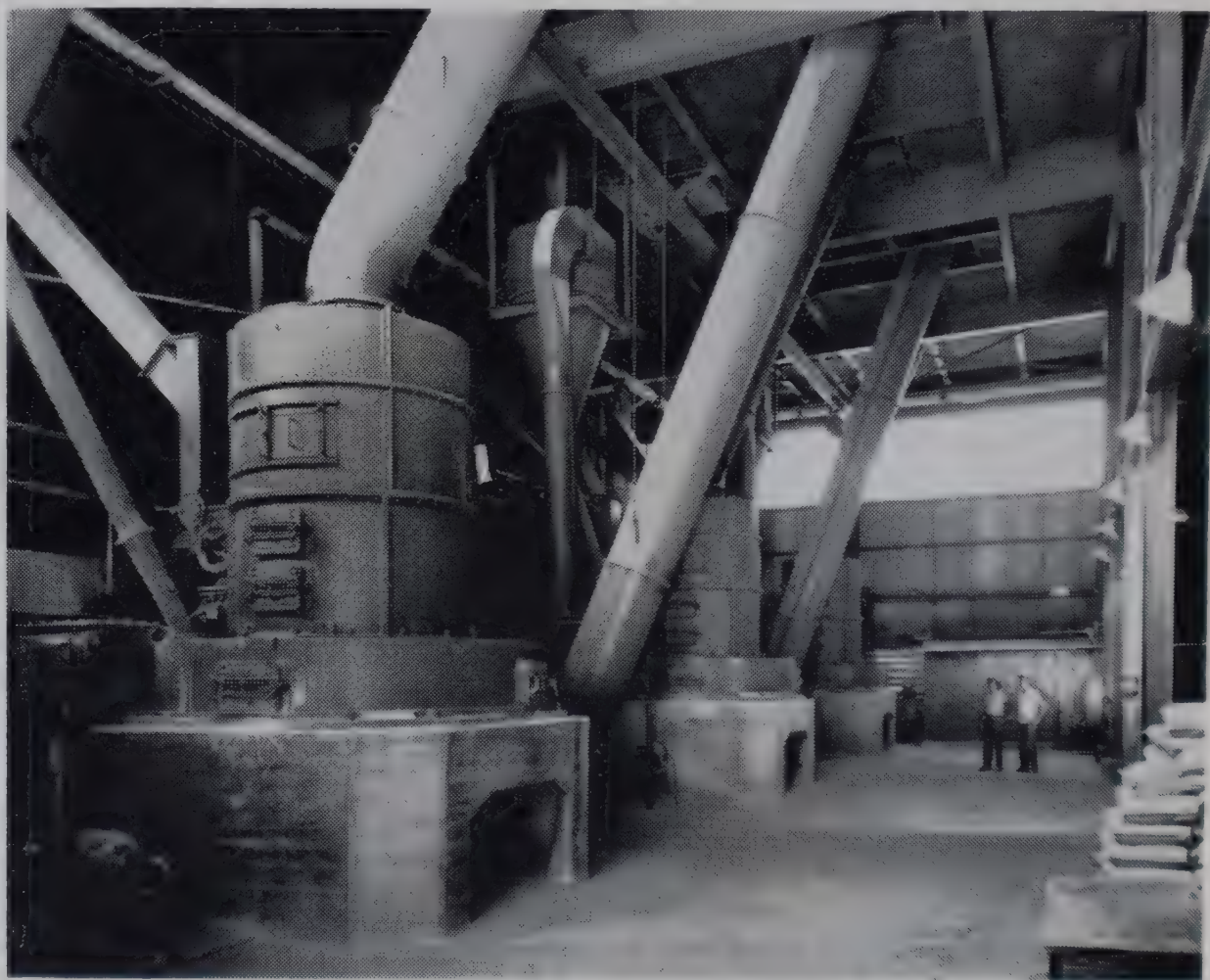
The slurry leaving the last acidulator goes by gravity to two blungers (17E), to which dry, recirculated fines are also being fed. The blunger is simply an inclined twin paddle mixer of extremely rugged construction in an enclosed steel shell. It is powered by a 100-hp. motor. Its purpose is thorough incorporation of the

slurry with recirculated fines. In effect, individual fines particles are coated with a thin film of slurry.

The blungers discharge by gravity directly into an oil-fired direct heat cocurrent rotary dryer (1E). In the dryer, reactions started in the acidulators and continued in the blunger are completed. In addition the moisture content is reduced to 2 to 3%. The temperature in the dryer is controlled to give a product discharge of 95° to 100° C. The dryer discharge moves by way of a conveyor, elevator, and double deck screens



Operating control floor of phosphoric acid section. Automatic rock dust feeder to reaction line



Interior of grinding plant right. Three Raymond mills

to storage bins for undersize, product, and oversize. Oversize is pulverized by swing hammer-type pulverizers (12E). Electric vibrating feeders (11E) maintain a steady flow to the pulverizers.

The pulverizers handle the oversized material and produce fines for additions to the blungers. The screens also separate fines for the blungers as well as material of proper size as finished product. The finished product passes by way of an overhead conveyor into the product storage building. The product is weighed continuously (14E).

Product Goes Out in Bags or Bulk. The granulated triple superphosphate is accumulated in piles in the storage building for a period of time long enough to allow sufficient cooling. The storage building is 150 X 325 feet with a capacity of 35,000 tons.

The product may be bagged in 80- or 110-pound paper or burlap bags. It may also be shipped in bulk by way of box cars or cement hopper cars. In addition to its granulated product, Davison ships some pulverized triple superphosphate in both bags and bulk

To ensure longer lasting bags and easier handling a small portion of lime is added with the triple superphosphate at the time of bagging.

Supplementing its domestic shipments, Davison is now sending its triple superphosphate to Mexico, South America, Korea, and Puerto Rico. Export shipments go by rail to the Florida ports of Tampa or Jacksonville.

Analytical and Quality Control

Chemical laboratories on the site consist of a preparation room located in

the phosphoric acid section, a control laboratory in the triple superphosphate section and a main laboratory in the office and laboratory building.

In the preparation room, samples are reduced, crushed, and prepared for the control and main laboratory. Screen analyses are carried out here. In addition retained samples of production and shipments are prepared and stored here.

The control laboratory provides facilities for the rapid analysis of sufficient samples to:

- ▶ Maintain the gypsum in an optimum filterable condition.
- ▶ Keep extraction losses to a minimum.
- ▶ Keep washing losses at the filters to the lowest possible figure.
- ▶ Produce an acid of the proper strength.
- ▶ Minimize phosphorus pentoxide losses to waste.
- ▶ Maintain correct percentage of sulfuric acid in the reaction agitators.

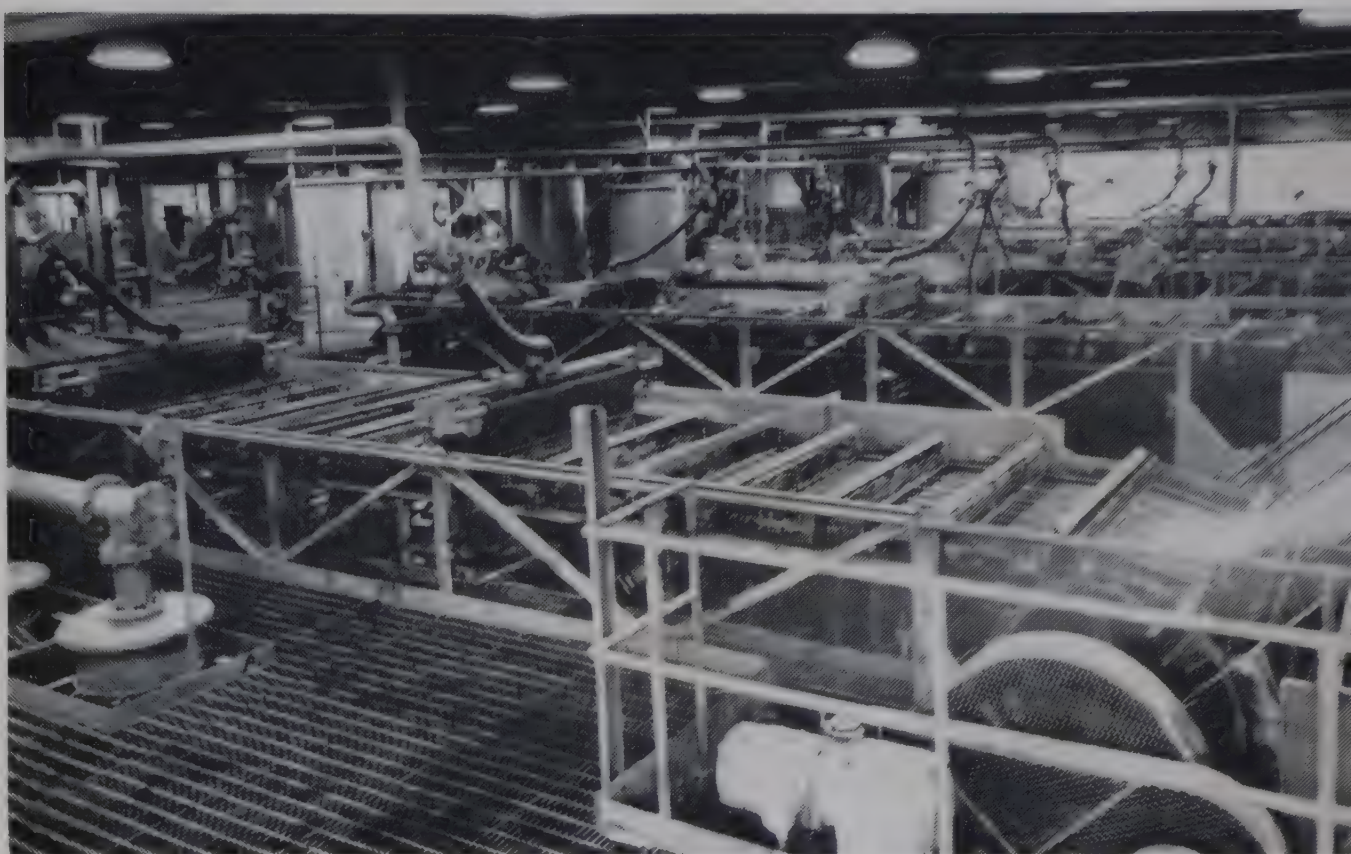
The main laboratory serves the phosphate rock mining operation as well as the triple superphosphate plant. Main laboratory functions as related to the triple operations are to:

- ▶ Certify quality of the product as produced and shipped.
- ▶ Check grade of raw material purchased.
- ▶ Maintain standards and setup procedures for control laboratory.
- ▶ Maintain records of plant operations from which daily and monthly operational efficiency and inventory may be gaged.

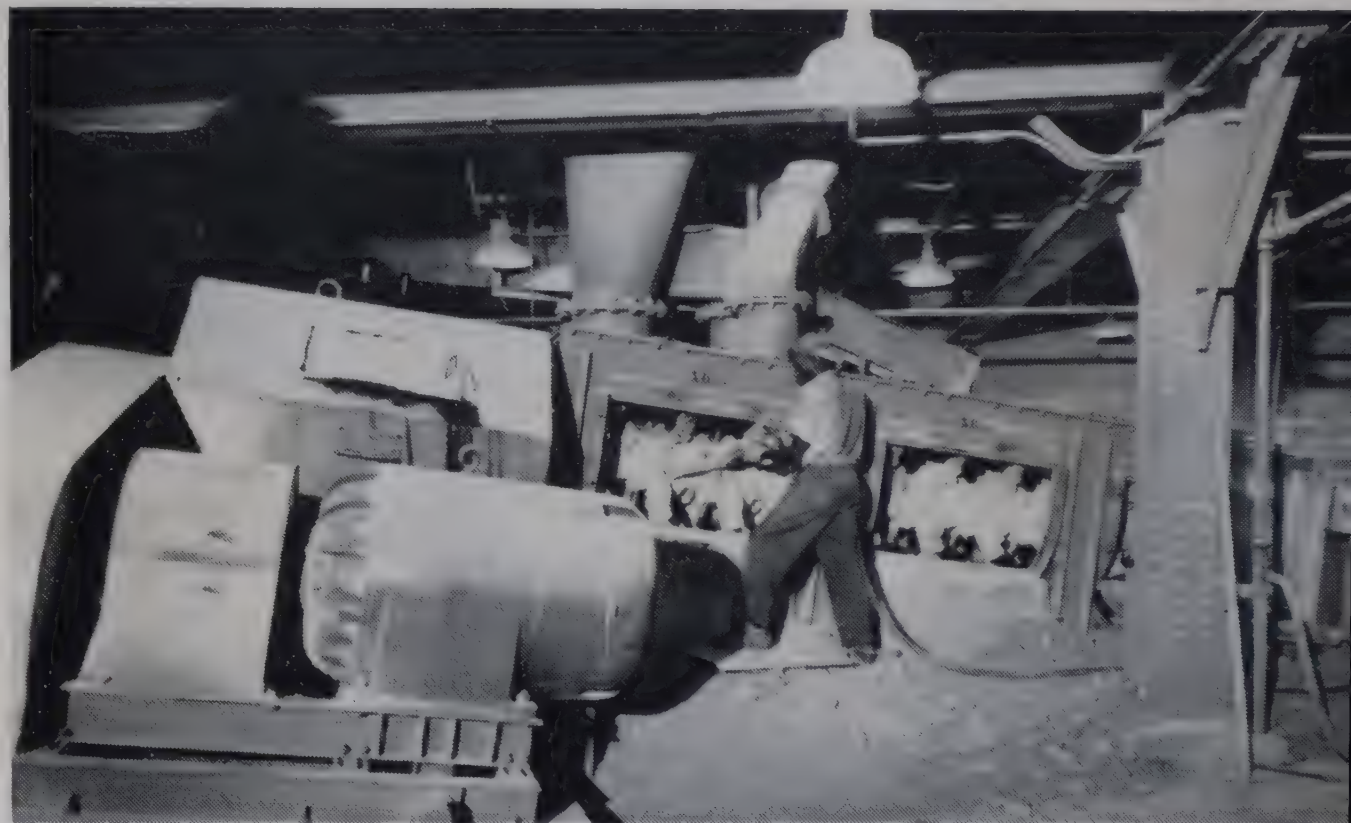
In an average week at the main laboratory over 550 samples may be run from the triple superphosphate plant. On these samples as many as 1300 determinations may be made. The most frequent and naturally the most important determination made on triple plant samples is for phosphorus pentoxide, P_2O_5 .

The results of critical analyses are plotted each day on control charts. Operating experience of more than 2 years has been required to judge just which analyses are significant and which vary enough to be plotted to control charts. Upper and lower limits of deviation (two sigma, 2σ) are shown on the charts and a green, red, yellow color code is used to indicate whether operation is normal, out of bounds, or border line.

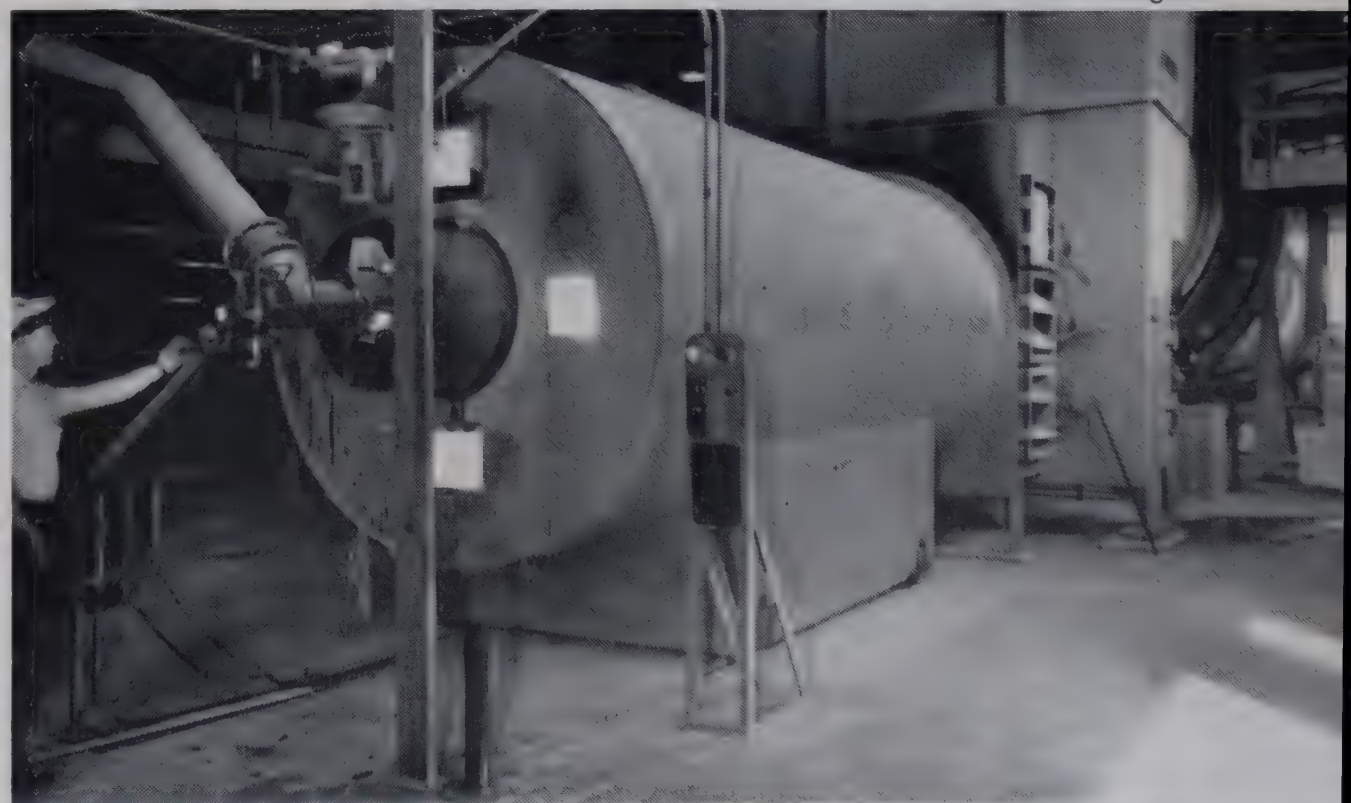
The control charts have proved to be important operational tools. They are kept up to date by a statistical clerk and continuously reviewed and interpreted by a quality control specialist. Weekly conferences are held to go over the control charts. Both the production and the maintenance departments are represented in the conference as well as the quality control engineer.



Filters

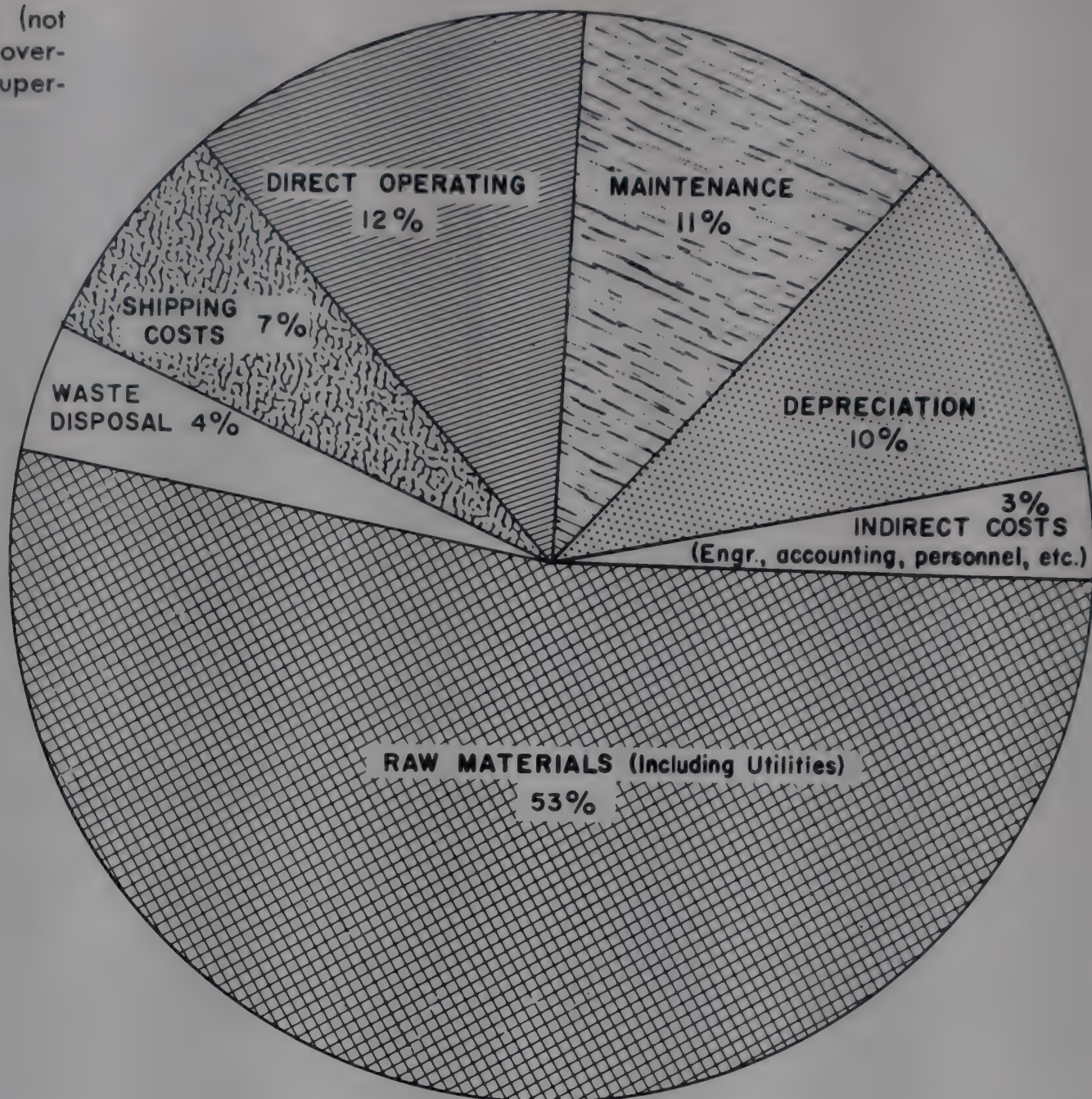


Blungers



Dryers

Cost breakdown. Plant costs (not including head office and selling overheads) for producing triple superphosphate



MAINTENANCE AND REPAIR

The very nature of the materials handled in producing triple superphosphate makes maintenance an extremely important consideration. The cost of maintenance is a significant factor in total product cost. In the Davison plant maintenance is under the direction of a maintenance superintendent who has reporting to him three maintenance supervisors and 48 craftsmen, helpers, and laborers.

The three maintenance supervisors have their responsibilities divided as to equipment. For example, anytime repairs are to be made on the grinding mills, one particular supervisor would be involved; repairs on the filters would come under the direction of another supervisor. The bulk of the maintenance work is done on the day shift but there are always at least two maintenance people on every shift.

With the parallel train design built into the Davison plant it is possible to carry out major repairs without interrupting the continuity of the operation. In the triple superphosphate section each train is shut down for 1 day in every month on a regular basis for preventative maintenance.

Important pieces of equipment that come in for regular maintenance jobs include:

- ▶ Acid evaporators. Boiled out whenever heat transfer or flow rates indicate fouling of tubes.
- ▶ Elevators. Bearings are inspected on every down day.
- ▶ Filters. Filter cloth thoroughly cleaned and inspected on every down day. Cloths may be patched or replaced as indicated.
- ▶ Blungers. Once per month bearing inspection, cleaning and paddle replacement where indicated. Air hammers are required to remove built up triple on paddle blades.
- ▶ Pumps and Motors. These are on a regular lubrication schedule with full time oilers responsible.
- ▶ Dryers. Complete inspection on every down day with particular attention to bearings and condition of inside flights.

Materials and Labor Required^a

Material or Labor	Av. Quantity
Primary rock (31.1% P ₂ O ₅), tons	1.20
Secondary rock (33.5% P ₂ O ₅), tons	0.46
Sulfuric acid (93%), tons	1.00
Wash water, tons	1.54
Fuel oil, gallons	7.1
Electricity, kw.-hr.	136
Operating and maintenance labor, man hours	1.9

^a To produce 1 ton of triple superphosphate.

Typical Analyses of Rock^a

	Per Cent by Weight	
	Primary rock	Secondary rock
Total P ₂ O ₅	31.1	33.4
CaO	46.0	47.1
Fluorine	3.6	3.5
Fe ₂ O ₃ and Al ₂ O ₃	1.6	1.7
Sulfur	1.3	0.2
Acid insoluble residue	8.7	7.6
Organic	1.8	..
Free H ₂ O on ground sample dried at 100° C. for 2 hours	1.1	0.5
+200 Mesh	37	22

^a Used in the Davison triple plant.

Typical Product Analyses

	Per Cent by Weight
Total P ₂ O ₅	48.1
Citrate insoluble P ₂ O ₅	1.8
Available P ₂ O ₅	46.3
Water soluble P ₂ O ₅	43.0
CaO	20.8
Sulfates	2.8
Moisture	3.2
Free acid (acetone extraction)	5.6
Fluorine	2.3

By using the control charts, supervisory personnel can see almost immediately results of any changes in operation. For example, increased losses over the filtration step can be picked up and steps taken to rectify it before it gets too far out of control.

Corrosion

Both the phosphoric acid and the triple superphosphate unit operate under conditions of severe service (15). Considerable experience in designing similar plants gave the Dorr Co. the background required to minimize equipment failures due to corrosion.

Crude phosphate rock contains a high

percentage of silica and the resultant slurries are highly abrasive. Phosphoric acid solutions in themselves attack all but a few selected materials and this, added to the large volume of slurry handled and elevated temperatures encountered, introduced important design problems (6). The presence of sulfuric and hydrofluosilicic acid in many of the process liquids further complicated the problem. Volatile reaction products of hydrofluosilicic acid are especially destructive.

In the Davison plant, rubber tank linings have been used with success. In many cases tank bottoms are also lined with special acid-resistant brick. Karbate tubes are used in the heat chambers of the acid evaporators. Piping in most cases is rubber-lined although in some cases saran-lined pipe has been used. The waste launder is of wood construction.

The traveling pan filters are of Type 316 stainless steel construction and use polyethylene filter cloths. Life of the filter cloths is approximately 6000 operating hours. When minor leaks are found, the cloth can be patched to extend its life. Rubber hose has proved to be the best arrangement for handling the filter feed slurry. Most pumps are of Type 316 stainless steel; in addition some units have rubber liners.

Future

Triple superphosphate has an important advantage over ordinary superphosphate—it contains over twice as much phosphorus pentoxide per pound of product. For areas located at long distances from the source of production this advantage becomes particularly economically significant. During the decade 1939–49, the consuming areas showing the highest rate of superphosphate used were the West and East North Central states. These are the areas in which manufacturing facilities are insufficient to meet the local demand.

These areas also demanded a higher concentration in complete fertilizer mixtures. Minnesota, for example, requires a minimum of 27% plant food in a mixture before it may be registered for sale in that state. Triple superphosphate is required to formulate such high analysis mixtures.

The trend in concentration of total nutrients in fertilizer mixtures is up. In 1900 average plant food content of all mixed goods was only 13.9%; in 1955 it was 27.7%. This means bigger markets for triple superphosphate.

In recent years transportation costs have accounted for 10 to 14% of the value of the finished fertilizer at its point of application. Any further increase in transportation costs will be reflected in an accelerated switch to triple superphosphate.

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Processing Equipment

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WILLIAM Q. HULL

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GOLD PROCESSING

THE story of gold is as old as the story of man—in fact, its story runs like a linking thread through history. From early times, the ancients were attracted by its beautiful color, brilliant luster, and nondestructibility. As a result of its wide distribution in the sands and gravels of rivers, and its distinctive appearance, historians think that gold was the first metal to attract the attention of prehistoric man in far spread regions of the world (5).

From the caves of Neolithic man, and the treasures of Cleopatra and King Solomon, comes evidence of appreciation of gold in that day, and it financed the empires of Rome and Byzantium. Throughout history—and to the present time—nations have been built on gold and currency based on it. The story of its use is unique among metals because it can be traced almost without break. The treasures of gold found by archeologists provide a record of the important art of the goldsmith, but, far more important, they have given a guide to the state of civilization which nations and

racers had reached as the pages of history turned.

Though fascinating as they are, these and many other aspects of gold have been and must be told in other tomes. Here we are concerned with technological aspects of its present recovery from ore in which it occurs as a small fraction of 1%.

Gold is found in minute quantities in nearly every part of the world. Ordinarily, it is found in association with silver, the relative amounts varying. Ore is obtained from three widely different sources—quartz veins or reefs; placers of aluvial deposits of modern or ancient streams; and deposits from which base metals are recovered rendering gold as a by-product.

Table I shows estimated production of gold by countries in 1955. The Union of South Africa accounts for

over half of current world production, and has produced from 30 to 55% of world output each year since 1906 (Figure 1).

The Central Witwatersrand conglomerate reef in the Transvaal of South Africa was discovered in 1886. It was then that operations began which led to development of the most productive gold field in the world. The story of the Witwatersrand is almost in itself a history of technology. Here, the early crude outcrop workings of the pioneers developed into the deep level mines of today; early stamp batteries were replaced by tube mills; the first deep level boreholes delved into the earth's crust in search of gold; modern hoisting machinery was first introduced; and the cyanide method of gold extraction was applied and perfected.

The Central Witwatersrand reef,

Table I. Estimated Gold Production of the World^a in 1955 (7)

Country	Ounces Fine (1000's)	Percentage of Total
Union of South Africa	14,591	53.6
Canada	4,580	16.8
United States	1,913	7.0
Australia	1,050	3.9
Gold Coast	687	2.5
Southern Rhodesia	525	1.9
Philippines	415	1.5
Mexico	380	1.4
Colombia	380	1.4
Congo	370	1.4
Japan	300	1.1
Others	2,039	7.5
Total	27,230	100.0

^a Excluding U.S.S.R.

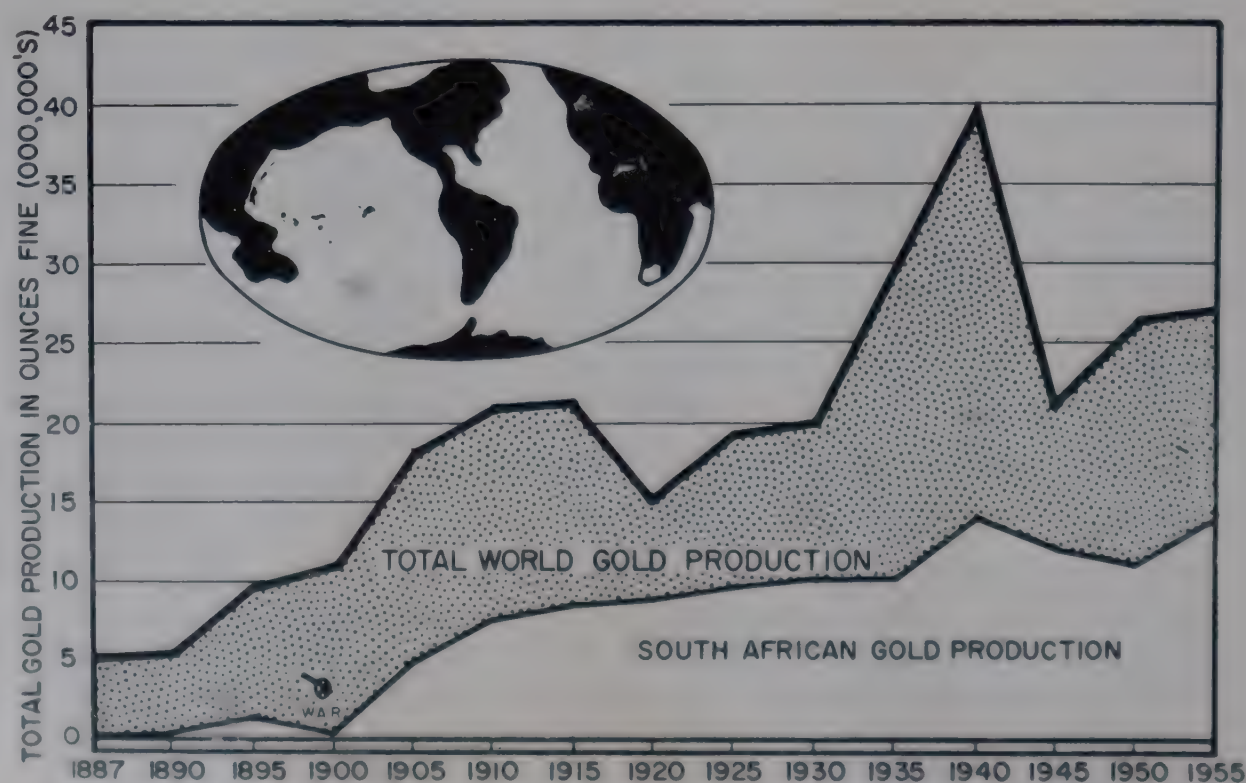


Figure 1. World gold production

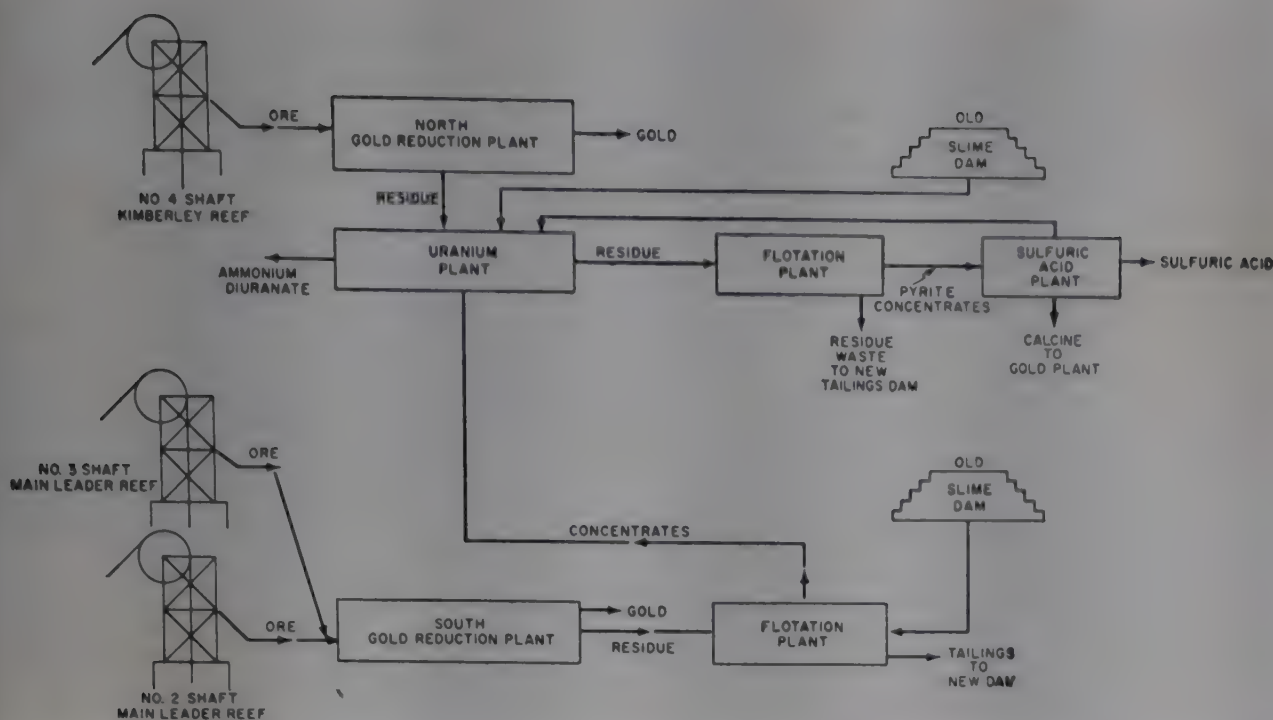


Figure 2. Interrelationships of Daggafontein Mine gold and uranium operations

later supplemented by discovery of the East and West Rand, led to establishment of South Africa's principal industry. In recent years, the discovery of gold in the Orange Free State, and the development of uranium industry based on mine tailings, have been the predominant factors in further industrial-

ization of South Africa. The uranium industry, which will be described in the next article in this series, came at a time when some gold mines were facing increasingly difficult financial problems and provided a needed stimulant to mines producing from deposits rapidly becoming uneconomical to operate.

Table II. Daggafontein Mines Ltd. Summary of 1955 Operations^a

Finance

Working profit	
Gold production, \$	10,236,862
Uranium and sulfuric acid production, \$	4,709,706
Total profit, \$	14,946,568

Gold production

Tons milled	2,658,000
Gold recovered, fine ounces	607,433.71
Yield, dwt. per ton	4.57
Working revenue per fine ounce, \$	35.46
Working cost, per fine ounce, \$	18.48
Working profit per fine ounce, \$	16.98
Working cost per ton milled, \$	4.23
Working profit per ton milled, \$	3.68

Ore reserves

Payable ore reserves, tons	12,678,000
Value, dwt.	5.32
Stoping width, inches	43.58
Inch, dwt.	232

Development

Total footage driven	47,512
Total footage sampled	41,410
Total footage payable	13,725
Percentage payability	33.1
Payable inch, dwt.	387

^a From the company's annual report to stockholders (South African Sterling converted to dollars at rate of \$2.80 per £ S.A.).

Table III. Basic Design Features of Reduction Plants

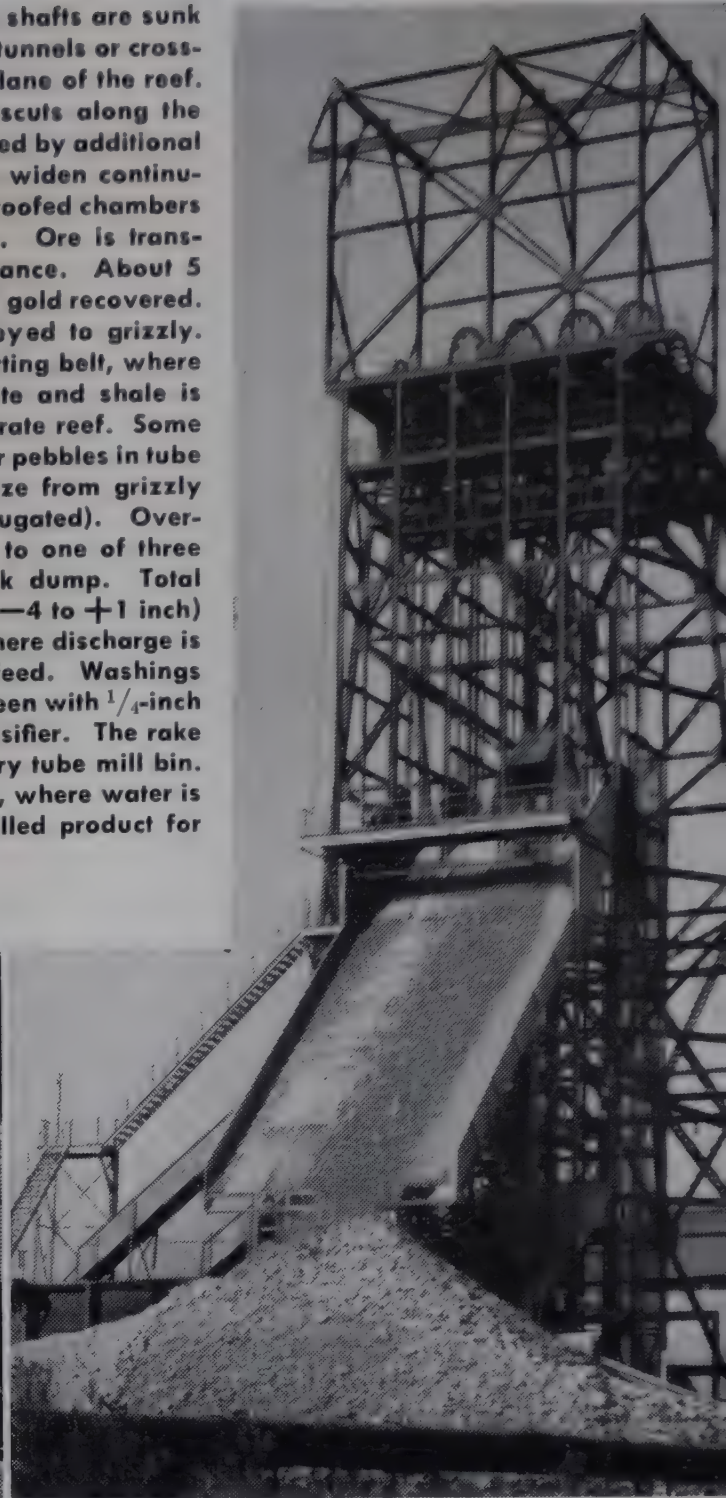
Plant	Daggafontein Mines, Ltd.		Orange Free State and Western Transvaal		President Brand Gold Mining Co. Ltd. Loraine Gold Mines Ltd.	Vaal Reefs Exploration and Mining Co. Ltd.
	South plant ^a	North plant ^a	Welkom Gold Mining Co. Ltd.	Western Holdings Ltd.; President Steyn Gold Mining Co. Ltd.; Free State Geduld Mines Ltd.		
Crushing	Single-stage; New-house gyratory crushers	Closed-circuit; Symons cone crushers and vibrating screens	Closed-circuit; Symons cone crushers and vibrating screens		Closed circuit; Symons cone crushers and vibrating screens	
Milling ^b	All pebble; three stages — primary, second, and semitertiary Reject pebbles system Hydrocyclones	Two-stage; primary and secondary pebble mills. Ball mills installed because of indication of insufficient large pebbles in mine ore to permit pebble milling ^b	All pebble; three stages; concentrating circuit incorporated in tertiary stage	Semitertiary circuit; continuous concentrators incorporated in mill	Three-stage pebble; continuous concentrators. Mechanical handling of pebbles for grinding media	Similar to President Brand and Loraine except all classification is done in hydrocyclones
Batch treatment	Batch or intermittent dewatering and slime collection followed by batch treatment in air-agitated tanks	Intermittent dewatering followed by batch treatment in air-agitated tanks	Similar to Daggafontein South plant with modifications	More extensive use of concrete Hydrocyclone classifiers in all except primary milling circuit All similar in design to Daggafontein North plant with modifications	Intermittent dewatering and treatment	
Filtration	Batch; Butters vacuum-leaf filtering plant	Continuous; rotary vacuum filters			Continuous rotary filters	
Steel balls	Pebble mills; to augment grinding capacity when necessary; worn-down grinding media as reject pebbles returned to crushing plant	Secondary mills; to augment grinding capacity when necessary. No reject pebble system required with primary ball mill			Both are combinations of Daggafontein North and South plants with modifications	

^a Buildings are largely steel and corrugated iron. In North plant, tendency is to replace timber used in South plant for upper floors, stairways, bins, launders, and pipes with concrete.

^b Ball milling costs about 16% per ton more than pebble milling, increasing total reduction costs by about 10%.



In gold mining practice in Witwatersrand, vertical shafts are sunk to gold-bearing reefs. From the shaft, horizontal tunnels or crosscuts, driven at various levels, meet the inclined plane of the reef. Other horizontal tunnels, called drives, are crosscuts along the reef line. Drives on succeeding levels are connected by additional tunnels from the reef plane. Raises and winzes widen continuously as ore is removed by blasting, forming low-roofed chambers or stopes—the main working place of the mine. Ore is transported to surface by highly mechanized conveyance. About 5 tons of ore are mined and milled for each ounce of gold recovered. From the stock pile, ore in South plant is conveyed to grizzly. After water washing, oversize ore passes to a sorting belt, where waste rock is hand picked and removed; quartzite and shale is easily distinguished from gold-bearing conglomerate reef. Some remaining coarse rock is used as grinding media or pebbles in tube mills; the balance passes to crushers. Undersize from grizzly drops into 9 cataract rollers (2 plain and 7 corrugated). Oversize from cataract is water washed and passed to one of three sorting belts. Waste is conveyed to waste-rock dump. Total waste is about 10% of the ore. Remaining ore (—4 to +1 inch) passes to one of four 7-inch gyratory crushers, where discharge is —1 inch and is conveyed to primary tube mill feed. Washings from sorting belts pass to (3 X 2 feet) vibrating screen with $\frac{1}{4}$ -inch mesh. Fines gravitate to a straight-line Dorr classifier. The rake product with the screen oversize passes to primary tube mill bin. Overflow from classifier is fed to a thickener tank, where water is recovered for re-use. Solids unite with final milled product for gold recovery



Several Unusual Aspects

The gold-mining industry of South Africa is unique in a number of ways. Producing a virtually fixed-price product, and having a ready market for its full output, the individual mining companies do not face competition in the usual industrial sense. Technological and cost-saving developments are freely shared and cooperation on all problems of individual companies is common.

The Transvaal and Orange Free State Chamber of Mines, organized in 1887, is an association of gold-mining companies furnishing services which can be more conveniently and economically provided on a cooperative basis. Among the functions of the Chamber of Mines are—negotiation for agreements with trade unions; preparation and administration of training and education schemes; attraction of labor; administration of social services and other workers' benefit schemes; industrial research; compilation of statistics; and publication of information on the gold industry. In addition, it operates a central gold refinery, a by-products

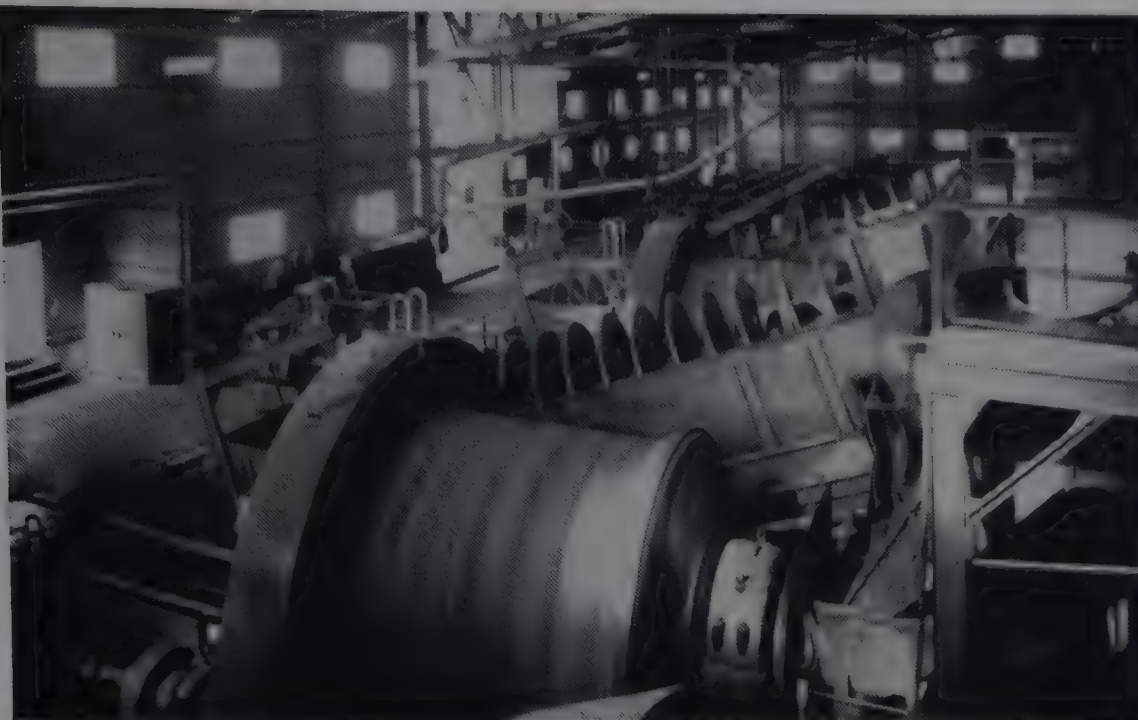
treatment plant, and certain laboratories for all its members and markets gold, silver and certain by-products, and, more recently uranium for them. The Chamber also expresses, when desirable, a common policy for the industry in regard to any of its problems. At the end of 1954, membership in the Chamber of Mines comprised 64 gold-mining members, including most of the more active mines.

Conglomerate Reefs

The geology of the Transvaal's Witwatersrand system has been described in great detail (6, 8). A more recent publication includes description of the geology of the deposits of the Orange Free State and differences in the two areas (2). It is suffice here to say that the gold occurs in highly siliceous conglomerate reefs at depths up to 10,000 feet below ground surface. The composition of the conglomerates includes in addition to the primary constituents a good proportion of secondary ones. Pebbles, chiefly of vein quartz, make up more than two thirds of the

conglomerate reefs. Also included are fine-grained quartzite pebbles, quartz porphyry pebbles, and smaller quartz grains. Chromite, osmiridium, and other materials are also present. Secondary constituents include quartz, sericite, and chlorite. Pyrite is the most common sulfide present and often makes up 3% of ore by weight. The gold, which is generally located in the conglomerates, is very finely divided and is frequently associated with some carbon.

Processing of the mined ore may be briefly summarized. At the reduction plant, the ore is washed, sorted, crushed, and milled. Resulting slime is treated with cyanide, which dissolves the gold. After being filtered from the nonsoluble rock, the gold-bearing solution is treated with zinc dust which precipitates the gold as a black sludge, a mixture of gold and zinc. This is collected, acid treated, smelted, and poured into bars. Further purification occurs at the Chamber of Mines refinery. The slime, from which the gold-bearing solution is separated, is pumped to slime dams, or, when uranium is recovered, to uranium plant receiving tanks.



Primary ball mills in North plant are made of $\frac{3}{4}$ -inch riveted steel plate with cast steel ends (IOE). The grinding load, 35 tons of 4-inch cast-steel alloy balls, is consumed at a rate of 2.6 pounds per ton of ore milled. Mills are equipped with hopper feeds and scoop discharge. Discharge screen, made of manganese steel, contains $\frac{1}{2}$ - to $\frac{3}{4}$ -inch tapered holes. All mills are horizontal. Each has a capacity of 1100 tons per day. Feed to primary ball mills includes the final crusher plant product, rake discharge from helical-screw classifier, and mill water, which is added to both feed and discharge to give a final 40% content discharge. Discharge is about 27% through 200 mesh. Each mill is in closed circuit with gravity flow, high weir, and helical-screw classifier, the sand discharge from which is recycled. Circulating load is about 2 to 1. Overflow from classifier is pumped to secondary mill hydrocyclone. Secondary tube mills, similar in construction to primary ball mills are operated as pebble mills (IIE); each has a capacity of 500 tons per day. Steel balls ($2\frac{1}{2}$ inches in diameter) at 400 pounds per day, are added to tube mill to supplement pebble grinding media; a 15% increase in capacity results. Feed to secondary mills is the underflow from hydrocyclone in closed circuit. Final cyclone overflow, 66% through 200 mesh, constitutes feed to gold recovery plant

Table IV. Screen Analysis and Sampling. Daggafontein Mines Ltd.

	Inches					+48	+100	+200	-200
	+1	+ $\frac{3}{4}$	+ $\frac{1}{2}$	+ $\frac{1}{4}$	- $\frac{1}{4}$				
Primary mill feed									
North	10.5	33.0	56.5				
South	13.2	9.5	27.8	18.3	31.2				
Primary classifier overflow									
North plant, 45% water						20.2	29.2	18.4	32.2
South plant, 40% water						28.1	27.0	17.4	27.5
Final product									
North plant, 88% water						5.4	28.6	66.0	
South plant, 82% water						3.8	24.8	71.4	

Ore from mine is - 10 inch grizzly size and contains approximately 8% +4 inch grizzly size.

Samples for plant control are taken at the following points—sorted waste rock (v), primary mill feed, primary classifier overflow, secondary classifier overflow and underflow, tertiary classifier overflow and underflow, secondary and tertiary mill outlets, final pulp (v), residue (v), unprecipitated solution (v), precipitated solution (v), filter wash (v), residue filtrate (v), mill circuit solution (v), return dam solution (v), bullion (v); (v) = samples sent to assay office for value determination. Additional samples are taken for moisture control. All solutions are tested for cyanide and lime content. Residues are assayed for both washed and unwashed values. Special samples of washing plant slime, gold slime, calcined slime, and mill inlet sand, are taken at irregular intervals.

Anglo American Group

The Anglo American Corp. of South Africa Ltd., was registered as a private company in South Africa in 1917. It was formed mainly as a finance and holding company and to undertake managerial, technical, and secretarial services. It has expanded its interests in mining to become, among other activities, the largest producer of gold. The corporation has considerable interests in the Union of South Africa, and Federation of Rhodesia and Nyasaland. Main interests in the Union are gold, diamonds, and coal mines. In the Rhodesias, Anglo American has copper mines, lead, zinc, and vanadium operations, and the only coal producing company. Several of the gold mines administered by Anglo American have been designated uranium producers and the corporation has

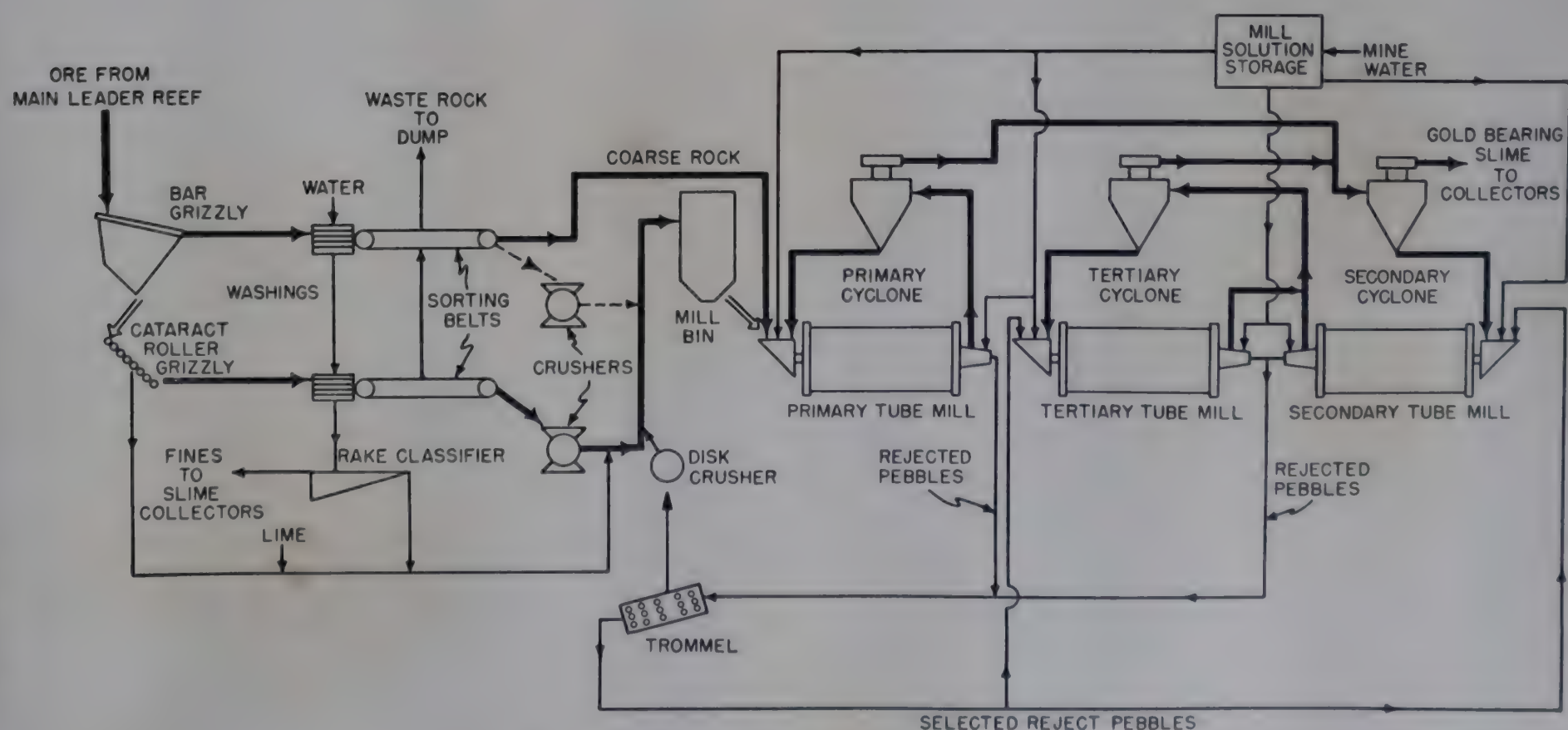


Figure 3. Ore milling, South reduction plant

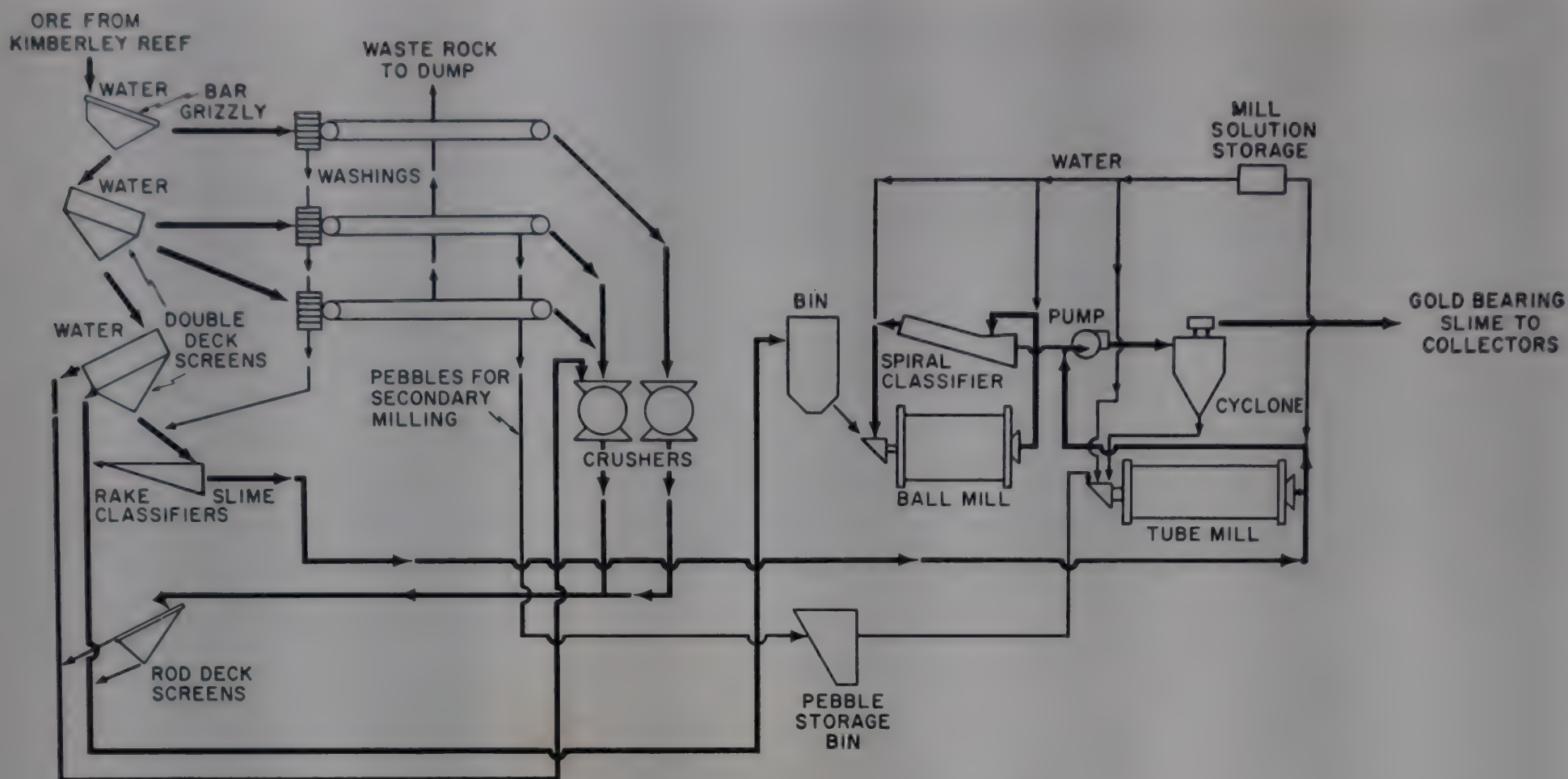


Figure 4. Ore milling, North reduction plant

played a key role in development of the uranium industry of South Africa. In the Transvaal, Anglo American has direct interest in eight gold-producing, prospecting, and developing companies and in the Orange Free State, seven. Of the total, eight are either producing uranium or are scheduled to become uranium producers.

Daggafontein Mines Ltd., whose history goes back to 1902, is the largest gold-producing company in the Anglo American group and one of the largest in South Africa (Table II). The company's operations include two gold-reduction plants, two flotation plants, a uranium plant, and a sulfuric acid plant which operates from concentrates produced in the gold-reduction and uranium plants. Operations of the several plants are intimately related and interrelationships are shown in Figure 2.

Daggafontein's South reduction plant, at the time of its construction in 1931, was an example of the most modern ore-milling and gold-recovery practices. The North reduction plant, built in 1948, incorporated later developments and other changes which were a result of the different properties of the ore treated. Features from the two have been combined in Anglo American plants built more recently in Western Transvaal and Orange Free State. Table III outlines the basic differences in the South and North reduction plants, and resulting design features in the newer mines in the Anglo American group.

Daggafontein became the first in the Anglo American group to produce uranium from the residual slime of its gold-reduction plants. In this article,

Daggafontein's reduction plants are described. In the next plant process article in this series, the uranium plant, with its manganese recovery and sulfuric acid production facilities, will be featured.

Mining of the Ore

The South and North reduction plants have designed milling capacities of 164,000 and 83,000 tons, respectively. Both plants are operated as all-slime plants, the final milled product being sufficiently fine that it is not necessary to remove sand for separate cyanide treatment, as is the case in a few older reduction plants. Both are batch in operation and the greatest part of the gold is removed through application of a conventional cyanide process. The two mills operate on a 24-hour basis, 6 days a week.

The South reduction plant processes ore from shafts 2 and 3 which operate on the Main Reef Leader at approximately 4800 to 5000 feet below ground surface. This reef, averaging 15 inches in thickness, is comparatively high in pyrites and gold content but low in uranium, and is inclined at a maximum dip of 14° to horizontal. In the mining area, the broken ore is scraped by winches into 1-ton cars, and transported along primary haulages by an endless rope system. At the shaft, the cars are tipped over a 12-inch grizzly into ore passes and the ore hoisted to the surface in 6-ton skips.

On the surface, it is necessary to sort the waste rock from that containing gold, and then reduce the gold-bearing ore to a size suitable for subsequent milling. In early days of the Witwatersrand, fine

crushing was carried out by stamp-mills using screening of 1000 holes or more per square inch. No stamps have been installed since 1918, but those erected prior to this time still play an important role in ore production. In the South Daggafontein plant, modified three-stage milling following crushing is employed (Figure 3). The circuit includes primary, secondary, and tertiary tube mills operating in conjunction with hydrocyclones as classifiers.

The use of hydrocyclones to replace conventional mechanical classifiers is a development that has taken place only since 1953. The development and use of cyclones in milling circuits in plants of the Anglo American group has been fully described (1). The advantages of their use over rake classifiers are:

1. Reduction in amount of gold locked in milling circuit
2. Improvement in differential grinding due to higher mineral concentration of the cyclone underflow
3. Reduction in maintenance cost
4. Minimum volume of pulp in circulation
5. Reduced labor complement, as result of elimination of greasers
6. Decreased opportunity for theft of gold concentrates
7. Lower accident risk

In summary, the advantages of this development have resulted in the substitution of cyclones for less efficient and more costly classifiers in many plants (Table III).

At the Daggafontein's South plant, the ore is first sorted and reduced in size in the crushing plant.

For satisfactory subsequent cyanida-

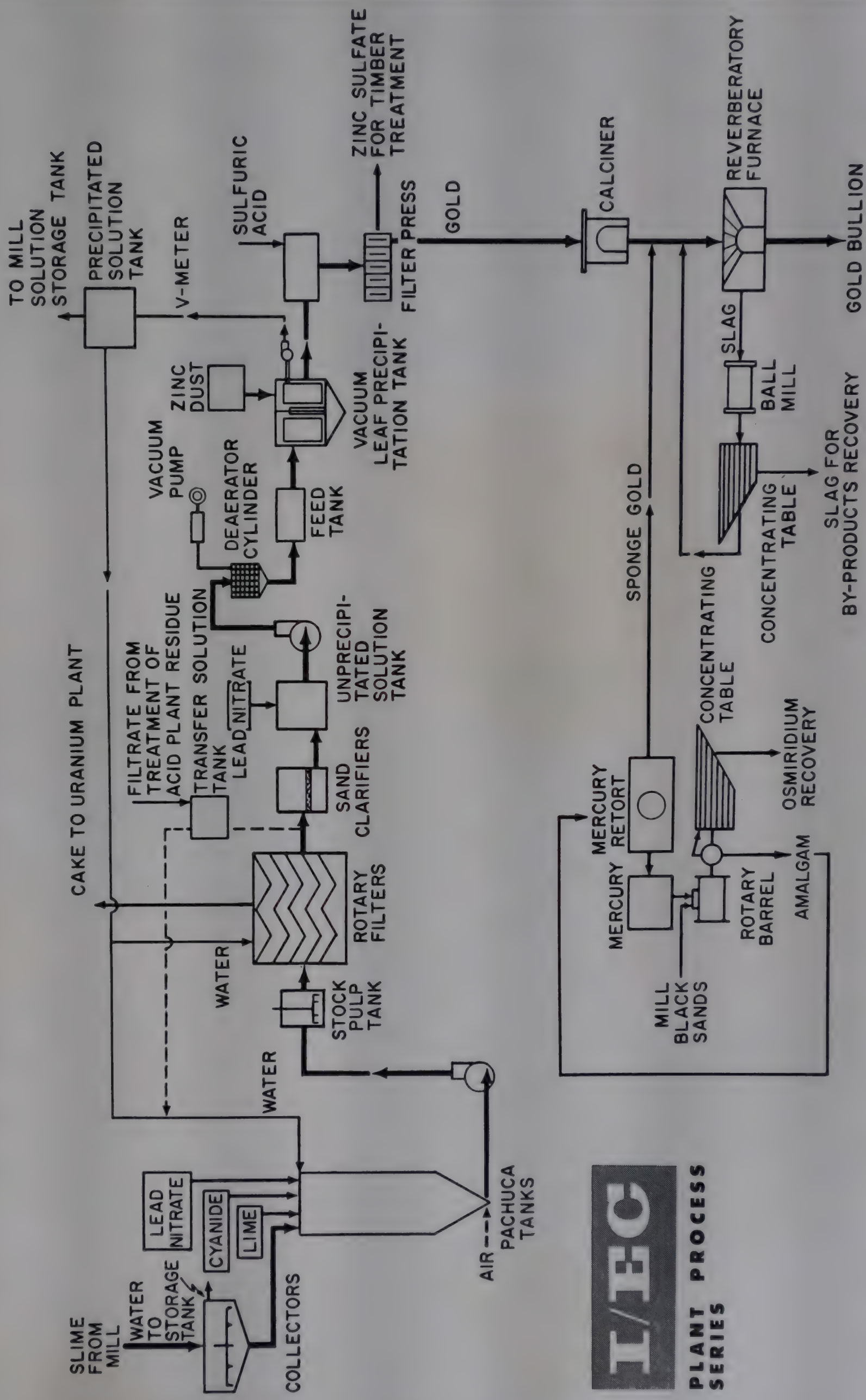


Figure 5. Flow sheet for gold recovery of Daggafontein Mines Ltd., North plant, Anglo American Corp. of South Africa, Johannesburg, S. A.

tion, the final milled products must be between 65 to 75% through 200 mesh (Figure 3). Table IV shows the screen analysis at the various points in the modified thru-stage circuit and of final discharge.

The principal items of the milling circuit consists of the equipment shown in Table V.

Feed to the primary tube mill includes coarse rock pebbles, crushed ore, underflow from the primary cyclone, and mill water added to increase the water content to approximately 23%. Discharge from the mill passes through screens with slotted holes about 1½ × 4 inches before passing to the cyclone. The material not passing through ½-inch trommels attached to the outlet trunnions of the mills, chiefly worn pebbles, is passed through another trommel with 1¼-inch openings. Pebbles not passing through the openings are used in secondary and tertiary tube mills. Undersize from trommel is passed to a disk crusher, the discharge from which is recycled to the mill feed.

Fines from the primary cyclones are pumped together with those from the tertiary cyclone to the secondary cyclones. Underflow from each secondary cyclone is recycled through the secondary tube mills. The overflow fines from these secondary cycle form the final milled slime which passes from the mill for gold recovery.

Primary and Secondary Milling

The North plant of Daggafontein operates from shaft 4 which delivers ore from the Kimberley Reef horizon. This reef is approximately 2850 to 3000 feet below ground, averages 23 inches in width, and is richer in uranium and gold content but lower in pyrites. The difference in the ore necessitates the use of a basically different milling plant, primary and secondary grinding only being required to produce necessary fineness (Figure 4).

Ore is mined, sized below ground to 10 inches and brought to the surface in a similar manner as that already described. It is passed over a 4-inch bar grizzly, where it is washed with water. Oversize (12% of the total ore) passes to a 42-inch wide by 70 feet long sorting belt. Grizzly undersize passes to two (10 × 5 feet) double deck vibrating screens, where additional washing is done (1E). First screen contains 2- and 1-inch square apertures. Oversize (-4 inch to +2 inch) representing 28% of the total ore, is conveyed to a 70 feet long by 36-inch wide sorting belt. The -2 inch to +1 inch material (20% of the total ore) is conveyed to a third sorting belt of the same size. Fines from the first screen (-1 inch) representing about 40% of the



Final slime from milling circuit contains about 82% water by weight. For economical cyanidation, moisture content must be reduced to at least 50%. Thickening is accomplished in conventional slime collectors. At North plant, slime is pumped to 7 collectors (70 feet in diameter by 10 feet high) equipped with conical bottoms. Solids settle to the bottom and after decanting the clear liquid is pumped as slime containing 35 to 40% water to Pachuca or agitating tanks (right). Clear water, overflowing and decanted from collectors gravitates to a storage tank, is recycled to milling circuit

total ore, pass to a second screen, which contains ½- and ⅜-inch apertures. The coarser fraction separated is conveyed to a crusher which is subsequently described. Finer fraction is conveyed to primary mill feed.

The -⅛-inch pulp, to which is added all other washings, is conveyed to an 18-foot 4-inch by 8-foot rake classifier (2E). Rake solids are conveyed to primary mill feed. Slime is pumped to secondary tube mill discharge.

Hand sorting is done at the three belts. Approximately 14% (540 tons a day) is removed as waste. In the Kimberley Reef, this is chiefly quartzite with very little shale. No pebbles are used in the primary milling circuit at the North plant and thus none are picked for this purpose. However, approximately 3% by weight are added to secondary mill feed and these are selected on the second sorting belt.

Coarse ore from the first sorting belt passes to a 10-inch gyratory crusher set at 1½ inches and with a capacity of 30 tons per hour (4E). Finer sorted ore is crushed in one of two 4 feet short head cone crushers set at ½ inch, each rated at 140 tons per hour (9E). The discharge from the two sets of crushers is passed to one of two (8 × 4 feet) rod deck screens in closed circuit with them.

All +½-inch ore is recycled; -½-inch material passing through the screens is conveyed to mill feed bin. The closed circuit is necessary inasmuch as a finer feed is required for primary ball mills as contrasted with pebble mills in the South plant. Higher crushing cost is a resulting disadvantage.

The North milling plant includes the following principal equipment:

Primary circuit	
Number of ball mills	3
Diameter × length, feet	9 × 10
Classifier type. Helical screw	3
Size, diameter, inches	78
Secondary circuit	
Number of tube mills	6
Diameter × length, feet	6½ × 20
Type classifier. Hydrocyclone	3
Size, diameter, inches	30

Of 15 Anglo American plants, 13 have replaced bowl classifiers with hydrocyclones in secondary grinding circuits in past 2 years. The remaining two are converting. At present, experiments are being conducted to determine feasibility of replacing the helical screw classifiers with 24-inch diameter 20° hydrocyclones. In all cases previous, reduced costs and improved results have justified this change. In the Daggafontein North primary circuit, where the flow through the spiral classifier is by gravity, econom-

Table V. The Milling Circuit

	Primary Circuit	Secondary Circuit	Tertiary Circuit
Number of tube mills	14	8	2
Length by diameter	20' × 6'6"	20' × 6'6"	20' × 6'6"
Hydrocyclone classifiers, diameter	12"	30"	30"

ics may not be as favorable for the substitution inasmuch as a pulp pump system would have to be installed to feed the cyclone.

A second experiment being conducted involves removal of iron by means of a spiked drum rotating in the pulp from the mill. Magnetism is induced to the spikes by two electromagnets. Removal of iron is desirable before pulp enters pumps; also, its removal prevents subsequent conversion to ferric sulfate and conserves acid consumption in the uranium plant, which is fed by the gold-plant residue. At time of preparation of this article, the economics of iron removal had not been established.

Collection, Agitation, and Filtration

Before the discovery of the solubility of gold in cyanide solution, the affinity of gold for mercury was utilized as a means of extraction. This affinity results in formation of an amalgam when the two come in contact and through application of heat afterwards, the gold can be separated and the mercury recovered for re-use. For sometime after development of the cyanide extraction process in 1890, as much gold as possible continued to be recovered by amalgamation during the milling process. The pulp was

passed over amalgamated copper plates with the coarse gold being caught by the amalgam. Tube-milled ore was also passed over amalgamated copper plates before returning to classifiers. For numerous reasons, amalgamated plates in tube-mill circuits were replaced by corduroy strakes in 1922 and the latter are still used in many plants. A strake of this kind consists of an inclined table covered with overlapping strips of pulp sifting cloth. The ribs are placed transversely to the downward flow of pulp, and the ridges retain a concentrate containing the free gold. Recovery of free gold in corduroy strakes is common practice in older plants in the Witwatersrand and in some new ones as well, and accounts for a good part of the gold recovered, but many make no recovery of gold during milling and depend entirely on its dissolution by cyanide treatment. Daggafontein falls in the latter group. The practice involved in slime treatment and gold recovery at the Company's North plant is described in detail, Figure 5, with only the basic differences in processing at the older South plant being mentioned.

The North plant employs batch slime treatment, which might be broken down into three principal stages:

Collection. Slime is collected and

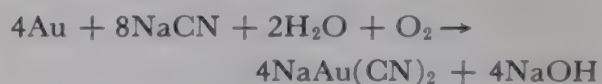
settled preparatory to dissolving its gold content in cyanide solution.

Agitation. Slime is air-agitated and gold and silver present dissolved in cyanide solution.

Filtration. Gold-bearing cyanide solution is separated from the slime, the solution passing to the precipitation plant.

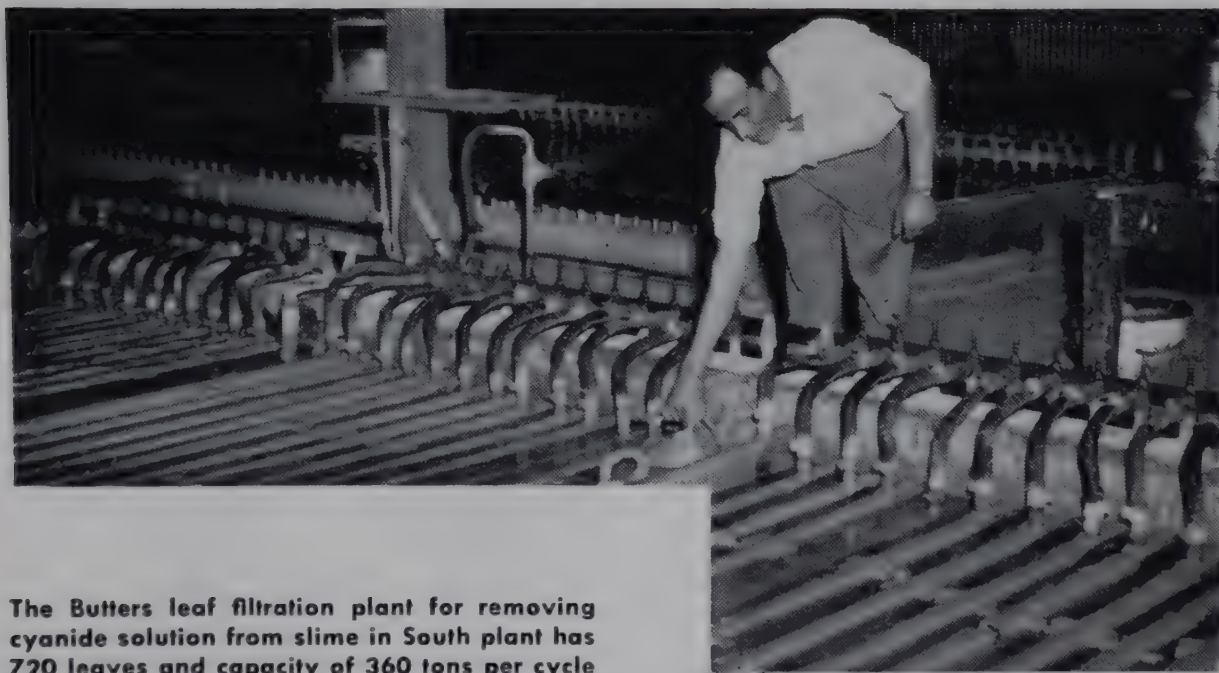
The essence of the cyanide process for treatment of gold-bearing slime is in the Pachucas, as here the gold and silver particles are dissolved from the slime for subsequent separation. At Daggafontein, there are 12 of these tanks, each 15 feet in diameter and 45 feet high, equipped with conical bottoms. As each tank is filled with pulp, compressed air at 35 pounds per square inch pressure is introduced in the bottom, keeping slime in a continuous state of agitation. Sodium cyanide is hand fed as a solid at rate of approximately 0.292 pound per ton of ore treated and dispersed through the pulp by the compressed air. The cyanide rapidly dissolves, forming a weak cyanide solution, strength of which is maintained at approximately 0.016% sodium cyanide. Agitation continues until all free gold is dissolved, the time varying from 10 to 16 hours.

Dissolution of the gold takes place according to Elsner's equation:



Oxygen required for this reaction is supplied by the compressed air used to effect agitation. The cyanide solution is stable only when alkaline. A degree of alkalinity is provided from the solution used to transfer the slime from the collectors. Balance is provided through addition by hand of powdered unslaked lime to the Pachucas, maintaining total alkalinity of 0.015 to 0.025% calcium oxide. Lead nitrate is also added in small amounts to precipitate any soluble sulfides present, permitting their removal during subsequent filtration.

The amounts of cyanide and lime re-



The Butters leaf filtration plant for removing cyanide solution from slime in South plant has 720 leaves and capacity of 360 tons per cycle (5E). In North plant, slime and gold-bearing cyanide solution passes to a stock pulp tank which feeds 7 (14 feet diameter by 16 feet long) continuous rotary filters operating under vacuum of 22 inches (6E). Drums are made of steel, and filter is faced with wood grids. Canvas (17 ounces) is held in place with 13-gage wire. Normal rotation speed is 2.5 minutes per revolution. Blow-off pressure is 10 pounds per square inch; discharge from drum has 27% water content. Each filter has a capacity of about 560 tons of solids every 24 hours. Cloths, scrubbed daily and treated with 2.5% hydrochloric acid, have a life of 180 days. Filter cake is normally pumped to large slime dams as waste. At North plant, it is repulped with water content of 45% and pumped to uranium plant. Waste from South plant is low in uranium and must be concentrated by flotation before uranium recovery. Some of the excess cyanide solution (at 0.002% potassium cyanide) is used in milling water circuit. Calcium oxide, 0.025%, is also maintained in mill solution for alkalinity control and flocculating requirements



quired for each tank are essentially predetermined. However, free cyanide content and per cent calcium oxide in solution are checked at regular intervals during agitation, additional cyanide or lime being added when required.

Upon completion of agitation, all gold and silver are dissolved in the weak cyanide solution which is thereafter removed from the slime. At Daggafontein's South plant, this is accomplished batchwise by filtering through canvas membranes by suction. In the North plant, variable speed, rotary continuous filters are used.

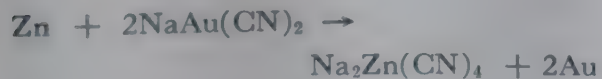
Precipitated with Zinc

After filtration, the dissolved gold and silver having been separated from the slime, their precipitation from the cyanide solution is required. Several methods have been developed for precipitation of the precious metals, among which the more important are (3):

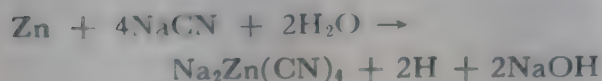
1. Filiform zinc (McArthur process)
2. Zinc dust (Merrill-Crowe process)
3. Electrolytic cell (Siemens-Halske and Tainton process)
4. Charcoal

The first three have been used on the Witwatersrand, the first two being in current use. All new plants employ the use of zinc dust, as does Daggafontein. The fourth method in which the ability of charcoal to extract 7% of its weight of gold from cyanide solution, without showing any change in appearance, is employed, has been used in some areas. While it has been investigated in the Witwatersrand, no reduction plants employ the process.

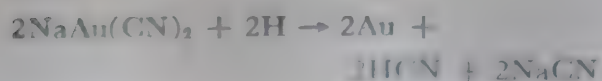
The chemistry of precipitation of gold by addition of zinc has been extensively investigated. Two principal theories have been accepted, in both of which silver is coprecipitated, as well as any copper present. The first theory explains the precipitation of gold as the result of the direct replacement of gold by zinc according to the reaction:



A second theory is that nascent hydrogen is produced by one of several reactions:



The nascent hydrogen then precipitates the gold:



In practice, the gold precipitation process may be divided into two stages—preparation of the gold-bearing solution and precipitation of the precious metals from it.

At the North plant, the filtrate from the rotary filters is passed through one of three (50 × 8 feet) clarifier tanks containing a 12-inch layer of sand. The sand rests on a timber grid which is topped first with a matting of coconut husk fiber, and, over that, a layer of jute. The clarifiers remove all colloidal matter and discharge is sparklingly clear. Sand in filter is scraped once in 10 days and replaced every 7 months.

(The calcined residue from the North sulfuric acid plant is also treated for gold recovery. The gold-bearing solution from its treatment, which will be described in the next plant process article, is also fed to the sand clarifiers at this point and joins the gold recovery stream.)

The crystal clear solution from the clarifiers is pumped to an unprecipitated solution tank. Here lead nitrate is added in order that the correct lead-zinc couple essential for good precipitation of the gold can be formed.

The precipitation of gold is a reducing process, and thus the excess oxygen added for the oxidizing dissolution process must be removed. Free oxygen also reacts with zinc forming zinc oxide, resulting in excess consumption of zinc and cyanide and decreasing precipitation of the precious metals. While chem-

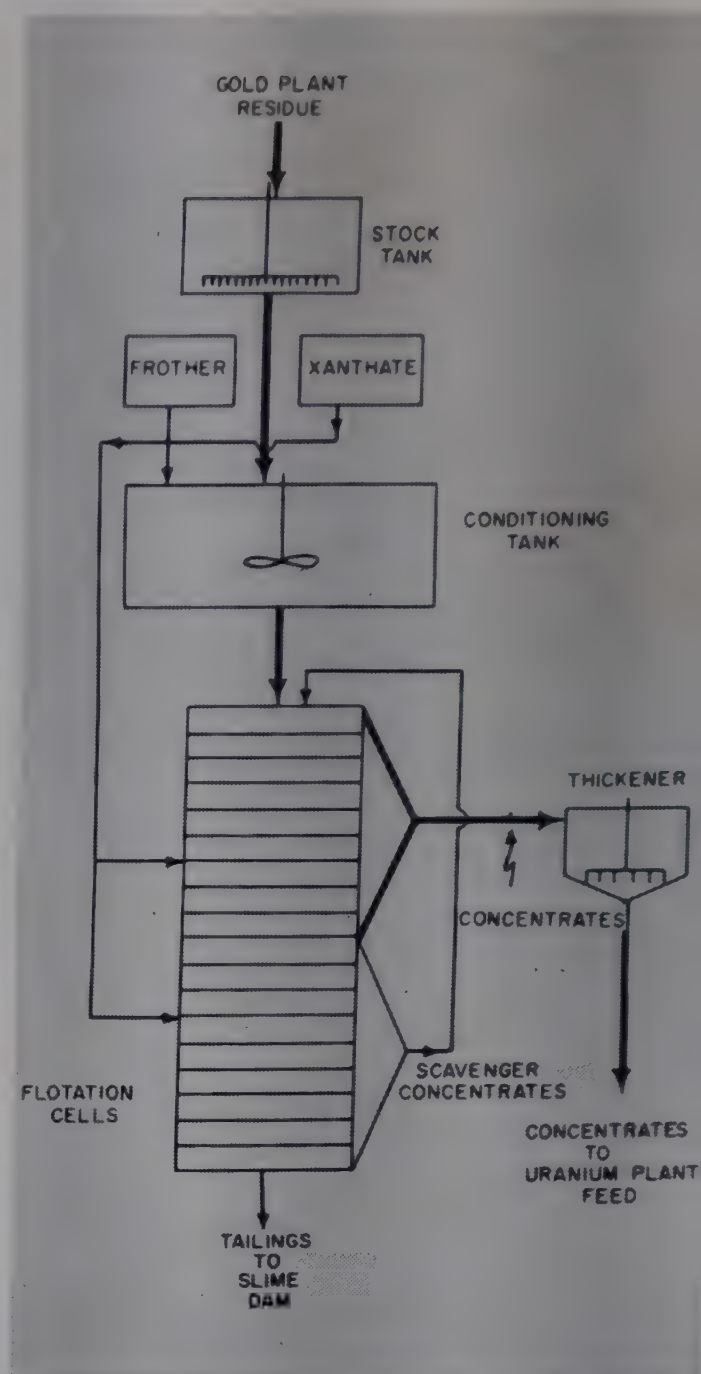


Figure 6. Flotation plant circuit



Flotation plant has 9 banks of flotation cells (3E), each bank having 18 cells—9 to produce finished concentrates and 9 for scavenger concentrates. Current and residual slime are fed to large stock tanks, from where it is pumped to conditioning tanks in flotation plant. Frothing agent is a mixture of 69% Frother 70 and 31% Aerofloat 25. Sodium butyl xanthate (10% solution) is used as a collector. The amounts of frother (59.0, 20.5, and 20.5%) and collector (57.0, 28.5, and 14.5%) are fed into the system at the conditioning tank, sixth cell, and twelfth cell, respectively. The overflow from first 9 cells, the final product, consists of iridescent gray-colored concentrates containing uraninite, iron pyrites, and gold. After thickening, it is pumped 2 miles to North Daggafontein uranium plant. Tailing pass to second group of 9 cells, overflow from which returns to first cell. Tailings from the 18th cell are pumped to a waste slime dam.



For smelting, fluxed mixture is placed in carborundum crucibles with fire-clay linings which hold 40 pounds of calcined slime or 290 ounces of gold bullion. Pots are charged into coal-fired reverberatory furnaces and temperature brought up to yellow-red heat (1100°C.). Fusion is allowed to proceed until the action has stopped, about 3 hours. Crucibles are removed from furnace and contents poured into conical cast-iron molds. When cool, bullion is separated from the slag, resmelted at same temperature in 1000-ounce batches, and poured into cast-iron bullion bar molds which are precoated with carbon deposit. When sufficiently cool, bullion bars are tipped from the molds, washed, dried, and stamped with an identification number. Two samples ($\frac{3}{4}$ inch deep by $\frac{1}{4}$ inch diameter) drilled from diagonal corners in opposite sides of the bars, are used for determining fine gold content of the bar



ical methods have been used, the dissolved air is normally removed by subjecting the solution to vacuum. This mechanical method, known as the Crowe process, is used entirely in new Witwatersrand plants. Daggafontein employs this process.

The cyanide solution is pumped to the top of a closed steel cylinder, 7 feet in diameter by 12 feet high, in which it flows downward over a wooden grid packing while exposed to vacuum of 22 inches (7E). Oxygen content is reduced from about 5 grams per liter to about 0.5 mg. The oxygen-free solution gravitates to the precipitation tank.

Gold and zinc concentrates from the

precipitation tank are periodically conveyed to an acid vat, where sulfuric acid is added to dissolve as much zinc as possible. The remaining gold is removed from the acid solution in a 30-frame filter press. Filtered gold slime is washed and air dried. It is general practice to roast the resulting slime to remove moisture and oxidize base metals present before smelting. This produces a high quality bullion.

At Daggafontein, these operations are carried out in a separate section of the extraction house which is always kept locked. This is general practice in the Witwatersrand and is designed to provide close supervision of the now highly

valuable material being processed. The filter-pressed gold slime is discharged into steel plate trays holding 150 pounds per tray and charged into a coal-fired calcining furnace holding 9 trays.

Calcination is carried out at a dull red heat (approximately 700°C.) for 16 hours, fusion being avoided. In this period, most base metals are oxidized, permitting their combination with fluxing agents subsequently added. The slime changes in color from black to brown during calcination.

A typical analysis of calcined gold slime (Table VI) shows the impurities to be chiefly lead and zinc sulfates (4):

Table VI. Analysis of Calcined Gold Slime

	Per Cent	Probable Combination	
		Metals	%
Gold	44.70		
Silver	3.82		
Copper	1.41	Lead sulfate	25.8
Lead	19.74	Lead sulfide	2.8
Zinc	8.98	Zinc sulfate	13.4
Iron	0.17	Zinc oxide	4.5
Calcium	0.35		
Sulfate sulfur	16.19		
Sulfide sulfur	0.64		
Silica	0.72		
Oxygen	3.28		
Total	100.00		

The calcined gold slime is now smelted, during which the basic metallic oxides present combine during fusion with the acid oxides of silica and boric acid of the fluxes used, forming silicates and borates.

Daggafontein used the following average proportion of fluxes:

	Parts
Calcined slime	73
Sand	17
Borax	8
Manganese dioxide	2

Based on parts per 1000, the fine analysis of the resmelted bullion bars generally runs in the order of:

	Parts
Gold	910
Silver	75
Base metals	15

The bullion is shipped in this form to the Rand Refinery for additional refining.

A small amount of gold remains in the slag separated from the bullion and is recovered. Slag is ground to -24 mesh in a small ball mill, pulped with water, and passed over a concentrating table. Recovered gold particles are recycled to the reverberatory furnace. Tailings are sent to By-Products Ltd., another subsidiary of the Chamber of Mines, for further processing.

Additional gold is recovered from the mill black sands collected from the tube mills during the relining process. These



Gold bars, each weighing about 1000 troy ounces (except top one), are placed in storage before sending to Rand refinery for refining

sands fill the interstices between liners and, due to the gravity concentration effect of the rotating mill, are rich in gold. These are amalgamated in a rotary barrel, the amalgam collected and the residue passed over a concentrating table. Mercury is recovered from the gold amalgam in a retort and re-used, and the sponge gold is passed to the reverberatory furnace. Osmiridium is recovered at the concentrating table, Daggafontein's production totaling approximately 33 ounces troy a year.

Slime Concentrated by Flotation

The South reduction plant treats ore, derived from the Main Reef Leader, which is a relatively low uranium bearer. It is necessary to concentrate the gold-free slime from the leaf filter plant before it can be used for uranium recovery. Concentration also enhances the iron pyrites content, which, after uranium recovery, is floated and the concentrate used for production of sulfuric acid.

The flotation plant (Figure 6) was placed in operation in 1953 and has a capacity of 10,000 tons per day. It treats, in addition to current slime from the reduction plant, recovered slime from tailing dams built up during previous years. The recovered slime is sluiced from the slime dams with high pressure water to a consistency of 61.5% water and pumped to the flotation plant, where



At North plant, two (11 feet diameter by 10 feet deep) precipitation tanks, Crowe-Merrill type, are equipped with 36 vacuum filter leaves arranged radially (each 7 feet high by 4 feet wide) (8E). Zinc dust is fed by belt conveyor to the deaerated solution. Agitation is provided by a slow moving propeller. As the gold precipitates, it is drawn to filter leaves where it builds up a cake along with excess zinc. Silver present is also precipitated and is subsequently separated at the refinery. Discharge from filtrate pump passes to precipitated solution through a V-notch measuring device. The amount of gold precipitated can be estimated from flow meter readings together with assay values of head and tailing solution. Filtrate is recycled for plant use. Twice a month, gold and zinc cake is removed from precipitation tanks and the zinc-gold slime, removed by a jet of water and brush scrubbing, is transferred to an acid vat

it is treated in ratio of approximately 1 to 1 with current slime.

Tables VII, VIII, and IX present data on the raw materials and services, gold recovery statistics, and monthly operating costs, respectively, for the Daggafontein Mines Ltd.

Final Refining of Gold

The Rand Refinery Ltd., a subsidiary of the Chamber of Mines, began operation in 1921 in Germiston near Johannesburg. Its chief purpose is the refining of all bullion produced in South Africa and the disposal of resulting gold and silver. The refinery is the largest of its kind in the world. Treatment of gold there is in itself a processing story, which is described here in very brief detail.

Bullion bars from the mines have an average assay value of 88% gold, 8% silver, and the remaining 4% chiefly copper, lead, and zinc, with small amounts of iron and other metals. The bars are weighed and two bars (2000 ounces) are melted in one of 32 coke-fired furnaces. The charge is melted in charcoal, more being added during melting to prevent oxidation of base metals and change in composition.

Melted bullion is poured into "slipper" molds so shaped in order that the ingots will properly fit into the crucibles used in refining. Carbon is added to prevent exposure of metal to air. When solidified, bullion ingots are removed and water

quenched. The ingots, weighing 400 ounces, go to the gold refining department.

The ingots are placed in pairs in clay crucibles and the crucibles set in a pot of graphite or carborundum. Borax is added in sufficient amount to cover the



At Rand refinery, molten gold is poured from crucible into a mold to form 400-ounce bar—last stage in refining process

Table VII. Raw Materials and Services

		Pounds per Ton Milled		
		North Plant ^a	South Plant	
	Cyanide	0.589	0.297	
	Lime	1.898	2.076	
	Zinc dust	0.060	0.050	
	Hydrochloric acid	0.024	0.070	
	Sulfuric acid	0.056	0.040	
	Lead nitrate	0.062	0.034	
	Steel balls			
	Ball milling	2.627	...	
	Pebble milling	0.742	1.402	
Electric Power ^b				
Kw.-Hr. per Ton				
		— 200 mesh		— 200 mesh
Crushing	2.033	3.088	1.248	1.644
Milling	17.063	25.921	22.380	29.840
Treatment	5.429	8.248	3.480	4.641
Total	24.525	37.257	27.108	36.125

^a Consumption of cyanide and lead nitrate here is high due to treatment of calcine from acid plant roasters.

^b Water consumption is approximately 200 gallons per ton, and is mainly water pumped from the mine.

Table VIII. Gold Recovery Statistics for 1955

Gold Recovered	North Plant	South Plant
Cyanide, oz.	282,241.70	305,291.95
Mill, oz.	2,380.23	4,216.00
By-products, oz.	437.51	680.47
Total, oz.	285,059.44 ^a	310,188.42
Yield, dwt./ton treated	5.596	3.742
Residue, dwt./ton treated	0.246	0.217
Original value, dwt./ton treated	5.842	3.959
Extraction, %	95.79	94.52
Tons treated	1,018,755	1,657,845
Cost, \$ per ton	0.742	0.518

^a In addition, the North plant recovered 12,186 ounces of fine gold from treatment of calcined pyrite.

charge, a cover is placed on pot, the pot is placed in coke-fired furnace, and slow melting proceeds.

When melting is complete, a clay pipe is inserted into the bullion and attached to a chlorine supply. Chlorine gas is passed slowly through the molten metal, all metals other than gold reacting to form their respective chlorides. There is a considerable increase in volume as silver

chloride forms and some of the molten chlorides are carefully baled out. End of refining is observed when capacity to absorb chlorine is greatly reduced, spurtling of the gas from the surface occurs, and free chlorine gas can be noted. Gas flow is greatly reduced at this point and continued for a short additional period. When refining is complete, usually at end of 3 to 3.5 hours, the metal in the crucible has reached an assay value of 995 parts of fine gold per 1000.

The chlorides are removed and the gold is reheated in a tilting furnace with a capacity of 7000 ounces. Gold is poured from the tilting furnace into molds of 400-ounce (troy) capacity. A hot flame of acetylene-air is played over the surface of the gold in the mold to retard cooling and thus prevent shrinkage cavity from forming. Flame also reduces back into the bar any minute traces of oxide which otherwise would form on the surface and deface the bar. When cool, the gold bars are removed from the molds, chilled, identified, and placed in storage for shipment. These bars have a final analysis of 995 to 996 parts of gold and 5 to 4 parts of silver, this being a purity accepted in all world markets.

Table IX. Typical Monthly Operating Cost

	South Reduction Plant		North Reduction Plant	
	\$	%	\$	%
Skilled labor	0.077	14.2	0.111	14.6
Unskilled labor	0.051	9.5	0.057	7.7
Stores	0.206	37.9	0.258	34.1
Journal expenditures	0.001	0.1	0.036	4.8
Steel balls	0.037	6.7	0.104	13.7
Electric power	0.109	20.1	0.097	12.6
Engineering labor	0.048	8.8	0.010	1.4
Assaying	0.006	1.1	0.014	1.9
Miscellaneous	0.009	1.6	0.070	9.2
Total	0.544	100.0	0.757	100.0

Note: This article appeared in *Industrial and Engineering Chemistry* in December, 1956

The metallic chlorides are further treated for first, recovery of small amounts of gold, and secondly of silver.

The Chamber of Mines also operates a second subsidiary, By-Products Ltd. Here gold-bearing by-products, such as slag, ashes, and sweepings, from mines not suitably equipped to treat such materials are processed for gold, silver, and speiss recovery, the latter also containing iridium, osmium, ruthenium, and platinum.

Acknowledgment

The authors express appreciation to the Transvaal and Orange Free State Chamber of Mines for its cooperation in supplying considerable statistical information used in this report. Acknowledgment is made also to J. H. Mortimer and R. J. Adamson of Anglo American's consulting metallurgical department for both their time and interest in supplying technical details and reviewing the manuscript, and to Daggafontein Mines Ltd.'s officials and staff who cooperated during plant visits.

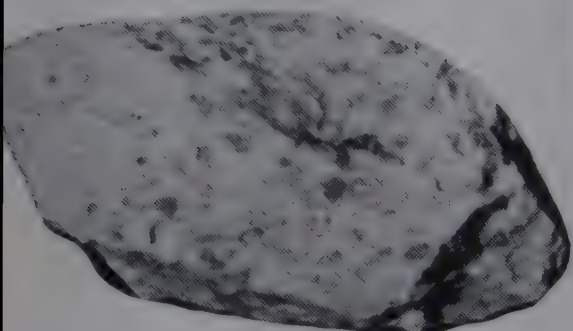
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Processing Equipment

- (1E) Bateman, Edward L., Johannesburg, S. A., Allis Chalmers double-deck vibrating screens.
- (2E) *Ibid.*, Dorr-Oliver rake classifiers.
- (3E) *Ibid.*, flotation cells.
- (4E) *Ibid.*, No. 1 S. F. Newhouse crusher.
- (5E) Fraser & Chalmers, (S. A.) (Pty.) Ltd., Johannesburg, S. A., Butters filtration plant.
- (6E) *Ibid.*, rotary vacuum filters, 14 feet in diameter by 16 feet long.
- (7E) *Ibid.*, Merrill-Crowe vacuum cylinder.
- (8E) *Ibid.*, Merrill-Crowe filters.
- (9E) Nordberg Mfg. Co. Ltd., Johannesburg, S. A., S. H. Symons crushers.
- (10E) Wright, Boag Head Wrightson (Pty.) Ltd., Johannesburg, S. A., ball mills.
- (11E) *Ibid.*, tube mills.

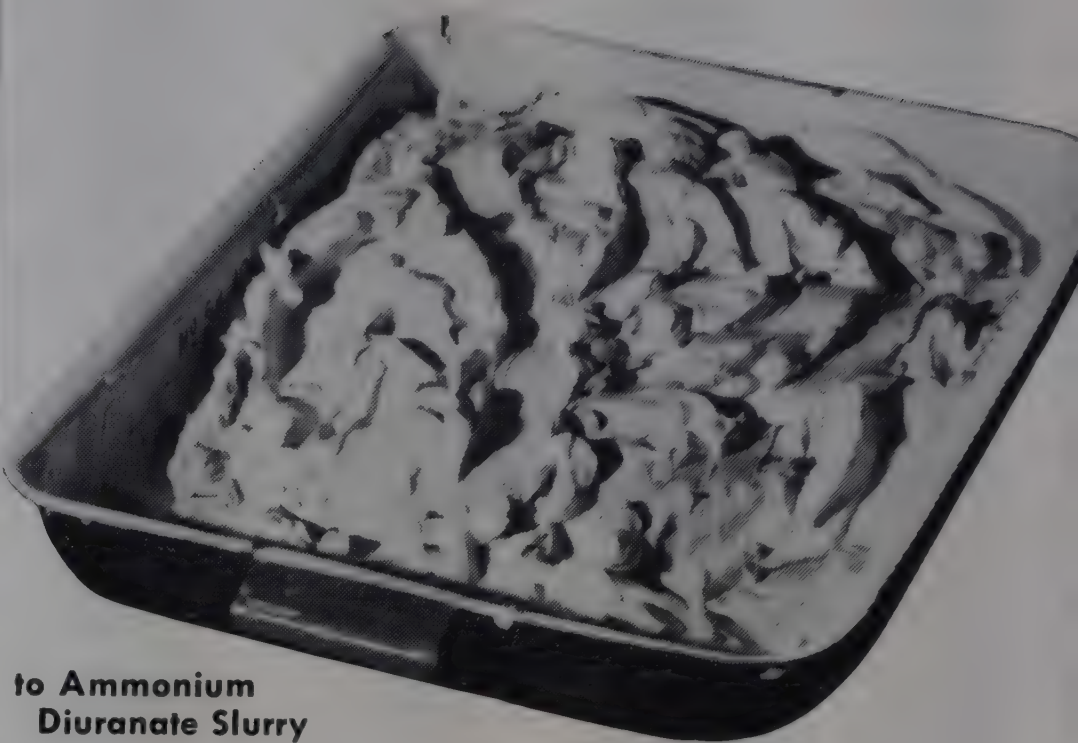
From Ore . . .



. . . to Uranyl
Sulfate
Solution . . .



. . . to Ammonium
Diuranate Slurry



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Uranium from Gold Wastes

URANIUM, one of the most important metals in today's atomic age, was discovered in 1789 by the German scientist, Martin Klaproth (7). During his discovery, Klaproth observed that a yellow oxide was formed, when an alkali was added to aqua regia in which pitchblende had been dissolved, and later identified it as uranium after the planet, Uranus.

Fifty years later, uranium metal was isolated from its salts by the Frenchman, Peligot, who heated uranium chloride with metallic sodium and dry potassium chloride. This method, with modifications, is still in use. While the late 1890's scientists, including Becquerel and Rutherford, were investigating radioactivity and nuclear fission, uranium remained a rarity until the ushering in of atomic fission and atomic warfare in World War II. Its importance has been intensified increasingly with development of power from nuclear fuels and with many other peaceful uses of atomic energy.

Uranium, found in practically every country of the world, accounts for

approximately 0.0003% of the earth's crust (2). It is an important constituent in nearly 100 mineral species and a minor one in about 50 others. The most important mineral is uraninite, UO_2 , or the less-well crystallized variant, pitchblende. However, there is production from a number of other minerals.

Minerals containing uranium are found in a variety of rocks formed in widely differing geological ages. Most uranium produced has been obtained from two types of formation. Crystalline rocks of the Pre-Cambrian shield areas are typified by important deposits in Canada, Belgian Congo, South Africa, and Australia. Younger permeable sediments are productive in the pitchblende-carnotite deposits of the Colorado Plateau and carnotite-tyuyamunite deposits in Russia.

Before 1952, most uranium was derived from rich primary deposits in Canada and Belgian Congo, which contain 1% or more uranium oxide (pitchblende), U_3O_8 . Uranium in these high-grade ores was recovered by simple mechanical and leach techniques and

was used chiefly as a source of radium. Since that date, when uranium became a by-product of gold processing in South Africa, many changes have occurred in uranium metallurgy and vast low-grade deposits, generally containing from 0.006 to 0.20% U_3O_8 , have been utilized increasingly.

Production of uranium from gold wastes when the Transvaal and Orange Free State plants (Table I) are in full operation will advance South Africa to a leading position among the world's uranium producers. Currently, the United States is the largest producer, South Africa a very close second, and Canada advancing rapidly.

In the early 1920's, corduroys, inclined tables covered with ribbed cloth, were introduced to recover free gold from ore in gold reduction plants of South Africa, replacing plate amalgamation. In 1923, Cooper reported that uraninite was present in minute quantities in the run-of-mine ore (3). In investigating corduroy concentrates he found that the uranium in the conglomerates of the Witwatersrand builds

Table I. Approved Uranium Producers in South Africa

Mining Company	Location of Uranium Plant	Date of Commencement of Plant
West Rand Consolidated Mines, Ltd.	West Rand Cons.	October 1952
Daggafontein Mines, Ltd.	Daggafontein	April 1953
Blyvooruitzicht G. M. Co. Ltd.	Blyvooruitzicht	April 1953
Western Reefs Explor. and Devel. Co. Ltd.	Western Reefs	September 1953
Stilfontein		
Ellaton		
Afrikander Lease	Stilfontein	September 1953
New Klerksdorp		
Babrosco		
Randfontein Estates G. M. Co. W. Ltd.	Randfontein	February 1954
East Champ d'Or G. M. Co. Ltd.		
Luipaardsvlei Estate and G. M. Co. Ltd.	Lulpaards Vlei	November 1954
Vogelstruisbult G. M. Areas, Ltd.	Vogelstruisbult	December 1954
President Steyn G. M. Co. Ltd.	President Steyn	January 1955
President Brand G. M. Co. Ltd.		
Free State Geduld Mines, Ltd.		
Western Holdings, Ltd.		
Welkom G. M. Co. Ltd.	Welkom	January 1955
Freddies Consolidated		
Loraine G. M. Co. Ltd.		
Harmony G. M. Co., Ltd.	Harmony	March 1955
Dominion Reefs (Klerksdorp) Ltd.	Dominion Reefs	June 1955
Virginia O.F.S.G.M. Co. Ltd.	Virginia	September 1955
Merriespruit (O.F.S.) G. M. Co. Ltd.		
Vaal Reefs Explor. and Mining Co. Ltd.	Vaal Reefs	May 1956
West Driefontein G. M. Co. Ltd.	West Driefontein	September 1956
Doornfontein G. M. Co. Ltd.		
Hartebeestfontein G. M. Co. Ltd.	Hartebeestfontein	October 1956
Buffelsfontein G. M. Co. Ltd.	Buffelsfontein	July 1957

Of 29 companies, there will be 17 uranium plants as of July 1957.

up in the slime rather than the corduroy product.

Extended searches for uranium during World War II resulted in recognizing the Witwatersrand as one of the largest low-grade uranium fields in the world. The historical and chronological investigations resulting were described at the Atoms for Peace Conference sponsored by the United Nations in Geneva in 1955 (8). Detailed surveys of world

uranium resources were also presented at that meeting (6).

In the conglomerates of gold-bearing reefs of the Witwatersrand, uranium generally occurs as free grains of uraninite of which the constituents are oxides of uranium. In some instances, it is closely associated with thucholite, a hydrocarbon of varying composition, containing thorium (very small content in South African ores), carbon, hydrogen,

rare earth oxides, and silica. Minerals containing uranium are present in almost all conglomerates in the Witwatersrand formation. The Main Reef series, which has been the principal gold-bearer, is a uranium bearer (4). Others, chiefly above but some below the Main Reef series, include the Elsburg Reefs and Kimberley Reefs.

In the previous article (4), approximately 5 tons of ore are processed for recovery of 1 ounce of gold. While the uranium content of ores in South Africa remains classified, it was indicated to be many times more plentiful than gold (8). The South Africa Atomic Act, adopted in 1948, with subsequent amendments, gives the State the ownership and right to prospect and mine all minerals containing more than 0.006% uranium oxide, U_3O_8 , or more than 0.5% thorium dioxide, ThO_2 , and the government grants authority for the mining and extraction of these materials.

The effluent slime of gold reduction plants in the past has been pumped to large slime dams for disposal. Accompanying the solids delivered to these dams are approximately equal weights of a cyanide-lime solution, containing some gold. As the solids settle out, some of the solution is reclaimed and returned to the reduction plant for recovery of part of its gold content and re-use of lime and cyanide. After development of the uranium industry, these dams at approved uranium producing plants have been reprocessed for recovery of uranium as is the slime from current gold reduction.

Uranium extraction can be divided into the same three stages as gold recovery—dissolution; separation of the solution containing uranium from other solids; and recovery of uranium from solution. The chief difference, however, is that gold processing employs alkali solution, whereas in uranium recovery, sulfuric acid solutions are used and acid resisting materials are necessary in construction of processing equipment.

Among others, two factors in development of the uranium industry of South Africa rate special note. Large amounts of sulfuric acid required were not available. As of 1956, eight sulfuric acid plants, utilizing pyrite content in the gold and uranium ore, were in operation or planned (Table II). These supply 1550 tons of acid per day and involve a total investment of \$21,000,000. Seven flotation plants were installed to concentrate the pyrites from uranium plant residual pulp (Table III), and these cost about \$9,000,000. Expansion of production capacity of limestone, lime, glue, nitric acid, and ammonia has also resulted, as well as electric power.

In addition to increasing supply of materials required in the new uranium industry, there was a serious problem of

Table II. Sulfuric Acid Plants Constructed to Supply Requirements of South African Uranium Industry

Mine	Capacity, Tons of H_2SO_4 /Day	Date Started
West Rand Cons. Mines, Ltd.	50	September 1952
Daggafontein Mines, Ltd.	220	March 1953
Western Reefs Explor. and Devel. Co. Ltd.	220	September 1953
Randfontein Estates G. M. Co. W. Ltd.	220	February 1954
Virginia O.F.S.G.M. Co. Ltd.	370	January 1955
Stilfontein G. M. Co. Ltd.	220	October 1955
Blyvooruitzicht G. M. Co. Ltd.	150	October 1956
Buffelsfontein G. M. Co. Ltd.	100	July 1957
Total	1550	

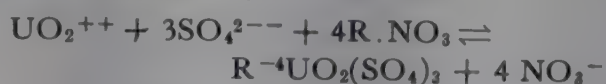
Table III. Pyrite Flotation Plants Constructed to Supply Sulfuric Acid Plants of South African Uranium Industry

Mines	Estd. Production, Tons of FeS_2 /Day	Date Started
Daggafontein Mines, Ltd.	180	April 1953
Western Reefs Explor. and Devel. Co. Ltd.	155	September 1953
Government Gold Mining Areas	325	May 1954
Vogelstruisbult G. M. Areas, Ltd.	90	December 1954
Virginia O.F.S.G.M. Co. Ltd.	150	July 1955
Harmony G. M. Co. Ltd.	70	January 1957
Buffelsfontein G. M. Co. Ltd.	75	July 1957
Total	1045	

developing a process for recovering uranium economically from solution. During 1946 to 1950, a number of possible chemical processes on Witwatersrand ore were investigated by Massachusetts Institute of Technology, Government Metallurgical Laboratory, South Africa, and U. K. Chemical Research Laboratory. None of the methods employing standard chemical means proved entirely satisfactory. Additional research in these laboratories, accompanied by work at Battelle Memorial Institute and Dow Chemical Co., led to the discovery of an ion exchange process, which resulted in a method to eliminate complex chemical separations and provided a simple method for recovery of uranium. A detailed history of the ion exchange process, including the technical problems and factors involved, as applied to uranium recovery has been published (5). Use of ion exchange to recover uranium from the acid leach liquors provides a selective method which gives almost complete recovery and is a great advance over chemical precipitation processes pre-

viously employed or considered. Other methods of treating leach solutions for recovery of uranium are shown in Figure 1 (1).

Numerous workers have shown that uranium in uranyl sulfate solution is present as the uranyl (UO_2^{++}) ion, together with undissociated uranyl sulfate (UO_2SO_4). A number of complex cations and corresponding sulfates are also present. When a pure solution of uranyl sulfate containing an excess of free sulfuric acid is passed through a strong base ion exchange resin in the nitrate form, the uranium is absorbed. For each UO_2 group absorbed by the resin, three SO_4^{--} groups are absorbed and four NO_3^- ions are displaced. The mechanism is shown by the reaction:



After being absorbed, the uranium is recovered by nitrate elution.

Uranium Producers

Daggafontein was the first company in the Anglo American group to produce

uranium from residual gold slime and is one of the largest producers in South Africa. Its uranium extraction and sulfuric acid units, costing \$11,000,000 began operation in early 1953. In 1954, estimated profits from the sale of uranium and sulfuric acid totaled \$4,000,000 and these increased to \$4,700,000 the following year.

Feed for the uranium plant comes from three sources—the final concentrates from pyrites flotation in the South gold plant, which is a product of both recovered and current slime from the South reduction plant; current slime from the North gold reduction plant; and recovered slime from the dams of the North reduction plant (Figure 2). They are approximately in the following amounts:

	Dry Tons/ Month	% Solids
Reclaimed slime from North plant	15,000	45
Current slime from North plant	90,000	50
Concentrates from South flotation plant	15,000	40

The three feeds are blended in an

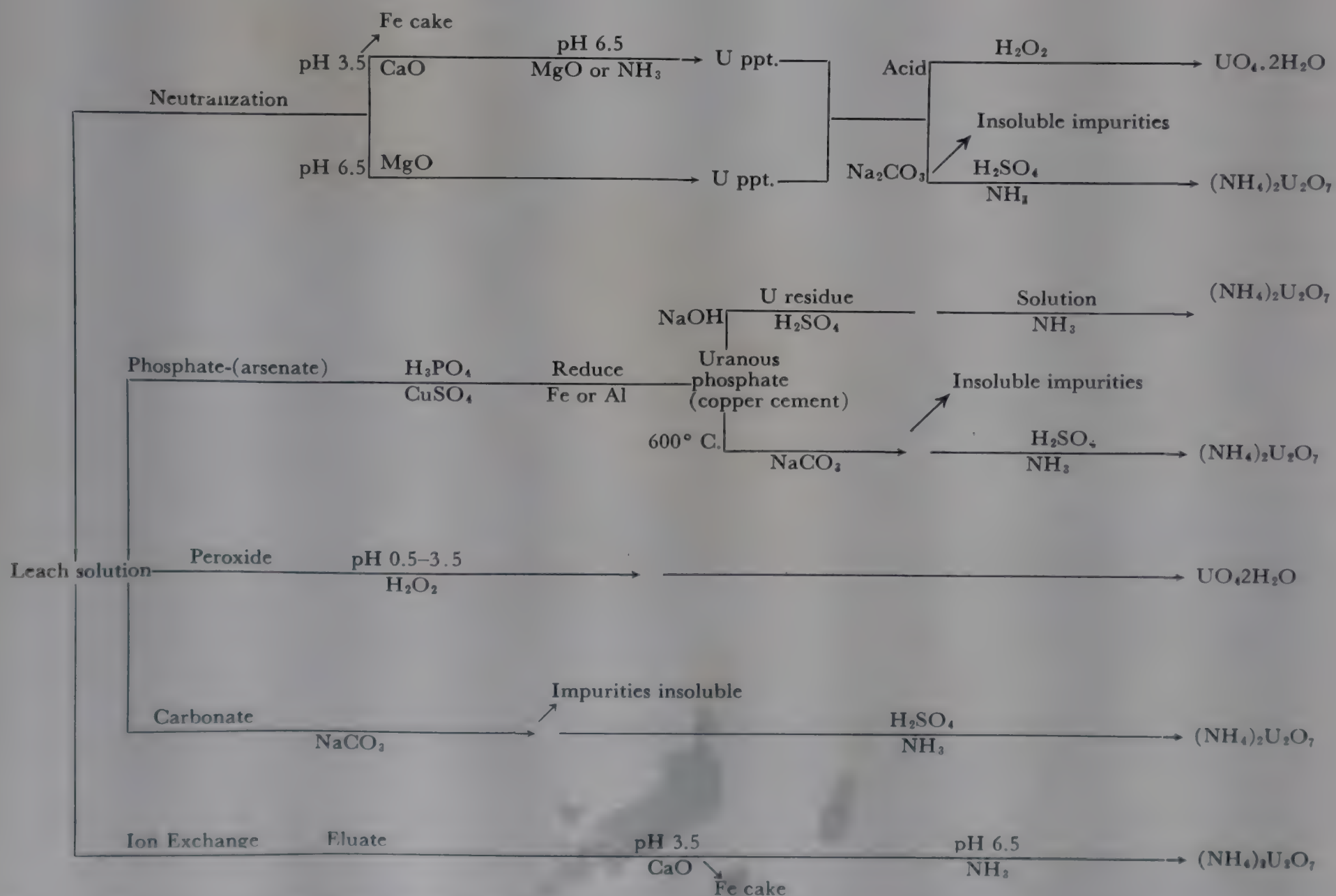


Figure 1. Recovery of uranium (1). When uranium leached from ore is present in a low grade solution with varying amounts of soluble impurities, the solution is treated to concentrate uranium content or remove impurities. When desired ratio of uranium to impurities is attained, uranium product is precipitated and converted to required oxide by drying and heating. Methods of treating solutions, in addition to anion exchange recovery, are

1. Direct precipitation in one or more stages by neutralization
2. Precipitation by phosphate or arsenate either as uranyl ion or after reduction as uranium ion
3. Direct precipitation with hydrogen peroxide under controlled conditions
4. Selective precipitation of impurities with carbonates



Nonacid rotary filters separate uranium containing pulp from solutions of gold waste and water used in hydraulic old slime dams



Uranium content is dissolved from gold reduction plant wastes in rubber-lined Pachuca tanks by adding sulfuric acid. Mixture is air agitated for several hours

elevated mild steel tank, 50 feet in diameter by 12 feet high. Mixed feed has a solids content of approximately 50%.

The feed includes in addition to the pulp, which contains the small percentage of uranium, large amounts of water used in hydraulic old slime dams, and cyanide and lime solution. Pulp is separated from these by nonacid rotary filters. In removing the lime and cyanide before the pulp is dissolved, acid consumption is decreased. In addition, certain salts, chiefly complex cyanides such as cobalt cyanide, and sulfur compounds, are removed which otherwise would seriously poison ion exchange resins used in recovering the uranium.

Blended slime from the main stock tank (specific gravity, 1.4) gravitates to eight nonacid rotary drum filters, 14 × 16 feet, constructed of mild steel (2E). These primary filters are arranged in two rows of four each with a 42-inch belt conveyor traveling between the two rows. Filters are equipped with fitted floats for the automatic control of level of pulp in filter pans. Suction is supplied by a battery of four 31- × 13-inch vacuum pumps with capacity of 2800 cubic feet per minute and driven by 100-hp. motors. Air for blow-off is supplied by low-pressure compressors delivering air at pressure of 10 pounds per square inch. Filter cloths are scrubbed every third day with a weak hydrochloric acid solution by rotary brushes turning at 130 r.p.m. Cloths are replaced at 30-day periods.

A fresh water wash is applied to filter cake to remove the compounds previously mentioned. Filters reduce the water content of cake to approximately 24%, filtrate being pumped to a reservoir for re-use. The cake must be repulped before adding acid to dissolve the uranium. It is carried by conveyors to a rubber-lined, twin impeller mechanically agitated repulper. Dilute sulfuric acid solution (filtrate from tertiary rotary filters later in process) is added to repulpers in amount to lower solids content to 60 to 65%.

The repulped material, containing a minimum of harmful impurities, is now ready for removal of its uranium content. It is pumped to a series of 10 rubber-lined Pachuca leaching tanks, 45 feet in over-all height and 22½ feet in diameter, the lower section being an inverted cone. Tanks are air agitated at pressure of 35 to 40 pounds per square inch with air being supplied by three high-pressure compressors. Approximately 0.70 cubic foot of air per minute is used for each ton of dry solids.

To the Pachucas are added acid, manganese dioxide which serves as an oxidant, and animal glue. Sulfuric acid (99%) from 1000-ton storage tanks, supplied by Daggafontein's own acid plant, is fed through a Rotameter from a steady head tank to the first Pachuca in series. Approximately 50 pounds of acid (100% basis) is used per ton of pulp. Manganese dioxide is metered as a water slurry (specific gravity, 1.4) at a rate of 12 pounds of manganese dioxide per ton of solids through a splitter-box to the second Pachuca in series. Slurry is prepared from pyrolusite ore containing 35 to 45% MnO₂, which is first ground in a ball mill (6½-foot diameter × 8 feet) to 72.5% of -200 mesh. About 90% of the uranium in the original ore is leached from the pulp in the Pachucas.

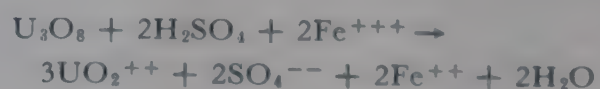
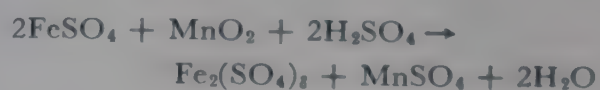
It is necessary to have an oxidant

present in addition to free sulfuric acid to dissolve uranium in the uranous form. Free iron, present from wear of grinding balls in ball and tube mills, reacts with sulfuric acid in the presence of manganese dioxide to form ferric sulfate thus assisting excess MnO₂ in its role as oxidant of uranium(IV).

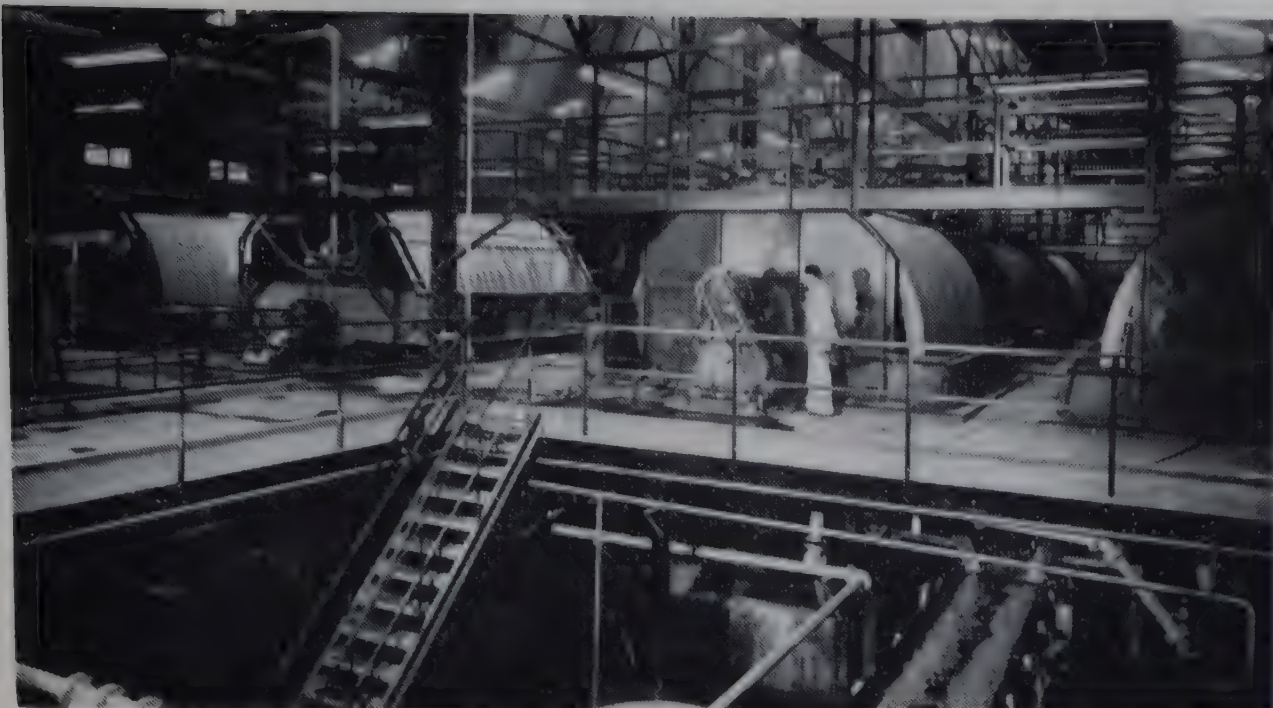
The order of adding acid and manganese is important. The ore contains reducing compounds, such as iron sulfide and metallic iron, which, when acid is added, generate hydrogen sulfide and hydrogen gas. If the oxidant was added at same time as acid, the reducing gases would consume a major part of the oxidant. Manganese dioxide is thus added several hours later so that all reducing gases formed by adding acid to pulp are evolved and removed.

The pulp is agitated in the Pachucas for 16 to 18 hours, by which time all uranium which can be economically recovered is in solution. Approximately 0.5 to 1 hour before filtration of the leached pulp, animal glue (10% solution) is metered by gravity into the pulp at rate of 0.45 pound per ton of ore. The glue serves as a filtering aid, and the timing for its addition is important as the maximum rate of filtration occurs within 0.5 to 1.5 hours following its addition.

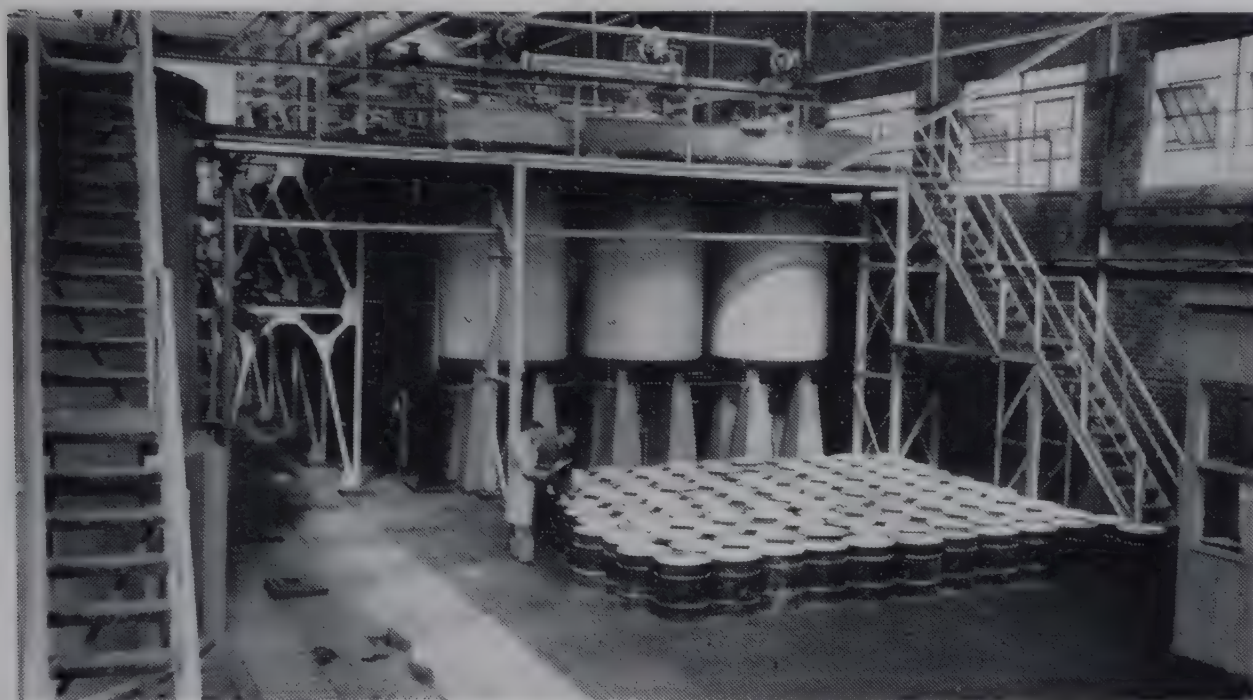
Reactions in the Pachucas can be shown by the following equations:



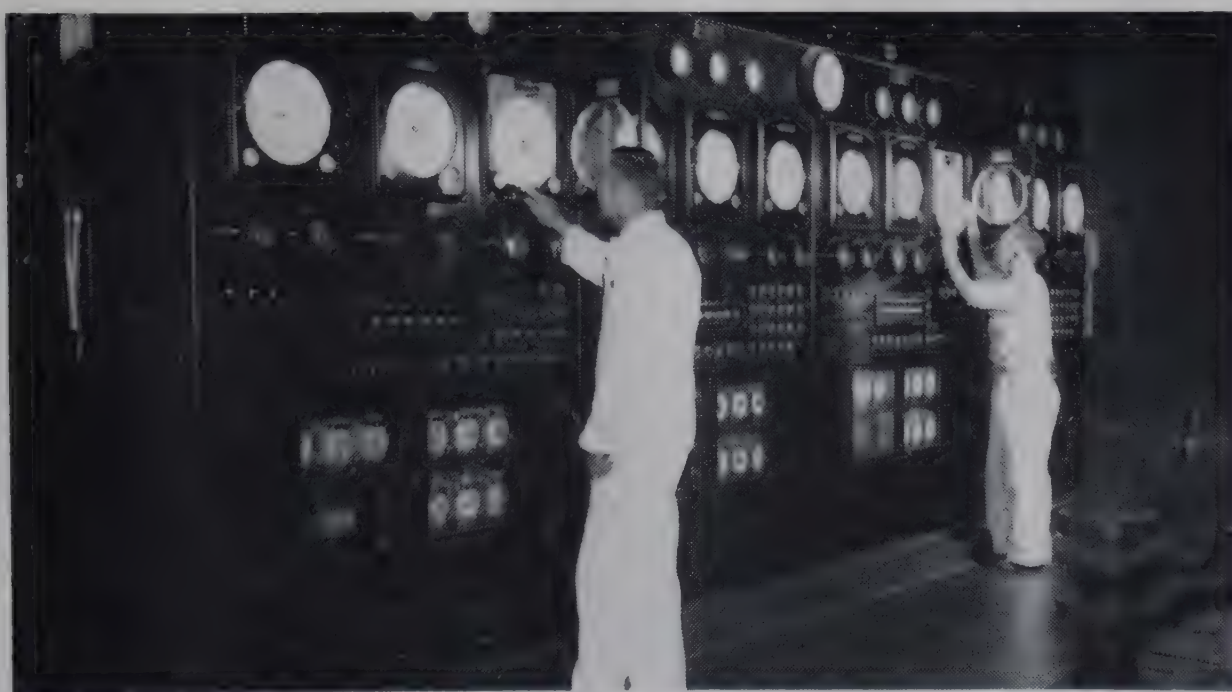
Effective operation of the entire uranium plant depends on proper control of the leaching process. Unusual care must be directed to leaching in this plant because of the three feeds, which require varying quantities of



Vacuum filters are used in separation of dissolved uranium from gold plant slime. Rotary filters, 24, are employed in primary, secondary, and tertiary separations at Daggafontein's uranium plant



Ion exchange plant, in which uranium in sulfuric acid solution is removed, consists of 12 columns, sets of 3 each operating in series



Complete instrumentation provides for automatic operation of ion exchange plant

acid and whose relative tonnages vary from day to day. Strength of the residual acid in the tanks must range from 4 to 6 grams per liter—a compro-

mise between two opposing factors. The free acid must not drop lower because, at lower concentrations, polythionates increase and poison the ion exchange

resins. At higher concentrations the absorption of uranium on the resins is affected.

Control of leaching is maintained by following tests:

1. Free acid content every hour in 1st, 3rd, and final Pachucas
2. Titrations for ferric and ferrous content as in (1)
3. Daily check on leach liquor for polythionates. (Concentration is kept below 40 mg. of sulfur, as S_4O_6 , per liter as column efficiency in ion exchange plant is seriously affected if content of 60 mg. per liter is reached.)

Uranium from Pulp

The next step is the separation of the uranium solution from the leached pulp. From the Pachucas, pumps delivering 640 gallons per minute, convey the 1.66-specific gravity mixture through 8-inch rubber-lined column to a rubber-lined elevated stock tank, 50 × 12 feet. There is a 1.5- to 2-hour delay in this tank, again emphasizing the importance of timing of glue addition. The pulp gravitates from the tank to a group of eight 14- × 16-foot canvas-covered rotary vacuum filters, acid-proofed in construction employing stainless steel and rubber (1E). They are similarly arranged in two rows of four filters each with a 48-inch belt between the two rows.

Vacuum is supplied by a battery of five pumps. A tertiary filtrate wash is applied. The filtrate, or pregnant solution, containing the dissolved uranium, is pumped to a settling tank in the precipitation plant where the uranium is recovered. Blow-off pressure on these filters is 4 to 5 pounds per square inch and average life of filter cloth is 60 days.

Filtering efficiency of the secondary filters is 75% leaving a significant quantity of uranium in the cake and this is recovered by tertiary-stage filters. Cake is diluted in rubber-lined repulper where dilution to 55 to 65% solids is effected by addition of water. Repulped material is pumped to a rubber-lined elevated stock tank, with a retention time of 1.5 to 2 hours, and is gravitated to a group of eight 14 by 16 feet rotary vacuum filters (2E). These are stainless steel and rubber in construction, similar to the secondary filters, and are similarly arranged.

A 48-inch belt conveyor carries the cake from these filters to a repulper where it is again diluted to approximately 63% water content. This cake contains the pyrites and is pumped to a 50- × 12-foot elevated stock tank in the flotation section, where its pyrite content is concentrated for use in the sulfuric acid plant.

The filtrate from the tertiary filters

is pumped to a rubber-lined storage tank and is used for dilution in primary repulper and for acid wash on secondary acid filters. If there is a surplus of tertiary filtrate, it is added to pregnant solution and is sent to the precipitation plant; if a deficiency, it is made up with water. All of the uranium previously dissolved in the Pachuca tanks (Figure 2) passes to the precipitation plant in the filtrate from the secondary filters. Too, all water added during repulping (except for the final stage) leaves the plant in this pregnant solution stream. A balance between the two must be maintained at all times.

The tertiary filters operate at a blow-off pressure of 10 pounds per square inch and average life of filter cloth is 70 days. Secondary and tertiary filters are scrubbed with water at 160° F. at rate of two per day in each section with rotary brushes.

Ion Exchange Recovery

The pregnant solution from the acid leach, or tertiary filtrate, is complex, containing the sulfates of acid-consuming constituents of the ore, cyanide compounds, silica, and the paramount—at this point—constituent, uranium.

Analysis of a typical solution shows the following:

Solution ^a	Grams/Liter
Fe ⁺⁺⁺	3.5
Fe ⁺⁺	0.5
Al ₂ O ₃	2.6
Mn	4.5
CaO	0.6
MgO	3.0
PO ₄ ⁻⁻⁻	0.2
As ₂ O ₃	0.2
SO ₄ ⁻⁻⁻	33.0
SiO ₂	1.0

^a Cu, Co, Ni, Cr, V, Mo, and Ti are also present in small significant quantities.

The uranium is present in the ionic form, UO_2^{++} . It is also likely present in complex forms such as UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{--}$, and $\text{UO}_2(\text{SO}_4)_3^{-4}$. The actual distribution of uranium is important in the ion exchange process.

In the precipitation plant, the uranium bearing solution is passed through ion exchange columns, where the uranium is absorbed as an anionic complex $\text{UO}_2(\text{SO}_4)_3^{-4}$. It is then eluted from the columns, filtered, and precipitated as ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, as which it leaves the plant in a thick slurry form.

At Daggafontein, the pregnant solution from the eight secondary filters first passes through a settling tank and

is then clarified through sand filters. The filtrate is free of all solid particles and is sparklingly water clear at this stage. It is pumped to a storage tank which feeds the ion exchange plant.

There are four sets of ion exchange columns operating in parallel, each of which consists of three columns, 12 feet high and 7 feet in diameter (Figure 4). The columns are made of mild steel and rubber-lined (3E). Each holds a 5-foot bed of strong base polystyrene quaternary amine ion exchange resin, Amberlite IRA-400.

In the operating cycle, two columns in series are used for absorption while the third is eluted in stages. The uranium and small amount of iron retained on the resin, and the effluent sulfuric acid or barren solution, containing no uranium but considerable amounts of iron and manganese sulfate, are passed to the manganese recovery section. The eluting solution used to remove the uranium complex from the resin contains a mixture of nitric acid (0.4N) and ammonium nitrate (0.6N).

Figure 3 shows a flow diagram of the Daggafontein ion exchange plant in

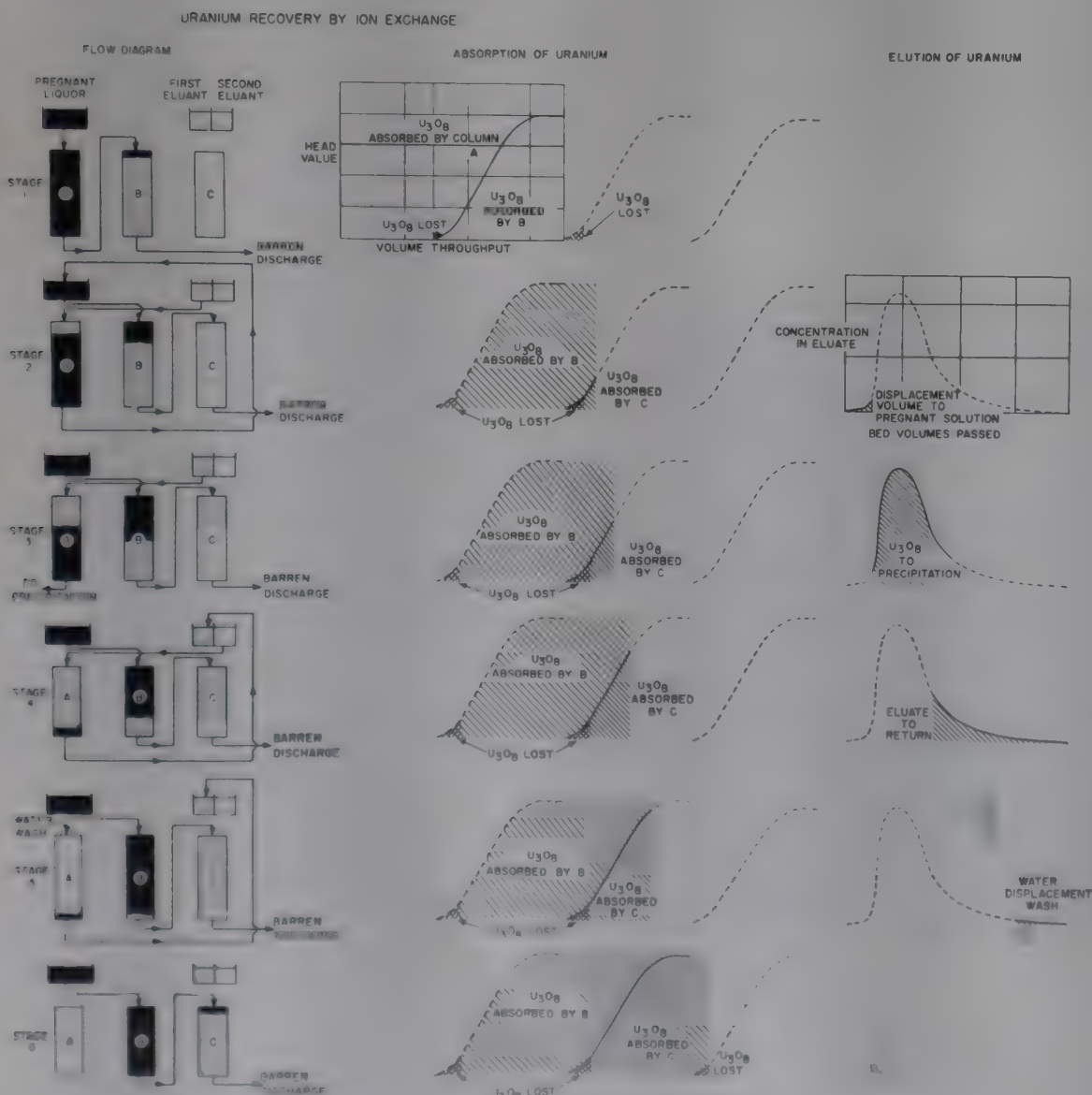


Figure 3. Uranium recovery by ion exchange

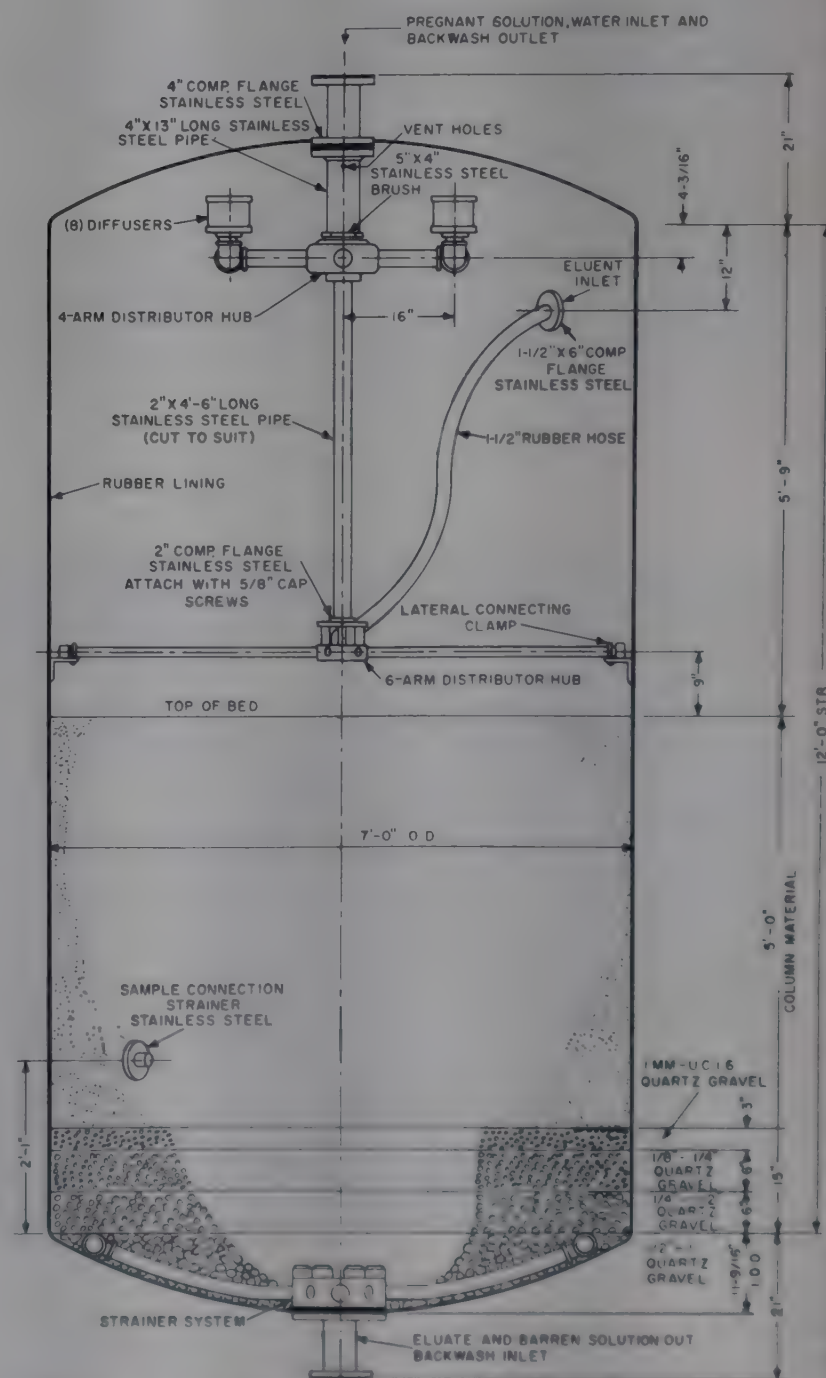


Figure 4. Schematic drawing of ion exchange column



After removal of iron, uranium is precipitated as ammonium diuranate in three agitated tanks operated in series



Final product of uranium plant is a slurry of ammonium diuranate containing 65% water

6 stages. In each case, the solid curves show the state of absorption in columns B and C, where absorption is carried out in series, and the stage of elution in column A, which has just been saturated at the beginning of the cycle shown.

Stage 1. At break-through point of uranium from column B, after absorption in columns A and B in series, column A has reached its maximum saturation. Flow of pregnant solution to column A is stopped. Pregnant solution which remains in A is displaced with a water wash through columns B and C. (Washing stage not shown.) No elution is conducted at this stage.

Stage 2. The pregnant stream flow is transferred to columns B and C in series in that order. The first partially used eluting solution is added to column A, displacing the wash water, and the stream is sent to the pregnant solution circuit. Absorption is increasing in column B and beginning in C.

Stage 3. The flow of eluant continues in column A and emerges as a rich uranium eluate, which is sent to precipitation plant. Absorption continues in columns B and C.



A candle filter is employed to separate precipitated ammonium diuranate



Ammonium diuranate slurry from uranium plant is conveyed by road tankers to central calcining plant where it is dried, extruded into pellets, and shipped to overseas users

Stage 4. After required quantity of first eluant has passed through column A, elution is continued with second eluant, which consists of pure ammonium nitrate-nitric acid solution containing no uranium. A portion of this eluate is sent to precipitation plant to maintain the volumes of first and second eluants in balance. The eluate from column A is then transferred to the first eluant tank for re-use.

Stage 5. The last of the eluate in column A is displaced from the column with water and the eluant goes to the first eluant tank for re-use. Absorption in column B is approaching saturation and uranium break-through from column C is near.

Stage 6. Column A is now ready for re-use and is left standing. Break-through has occurred from column C in the B-C absorption circuit, and column B is completely saturated and ready for elution. The cycle continues with absorption through C-A.

The final eluate from the ion exchange columns contains uranium together with a small amount of iron. The iron must be removed prior to precipitation of

uranium. The pregnant solution is stored in the strong eluate tank, 30 feet in diameter and 18 feet high. From this tank, it is pumped to the first of three 5- × 5-foot cylindrical rubber-lined agitating tanks. In the first, lime slurry is added to neutralize essentially all of the free acid present, and pH is adjusted in the last agitator to 3.5 with ammonia gas. Iron present precipitates as $\text{Fe}(\text{OH})_3$, ferric hydroxide, which is settled in a thickener, 25 feet in diameter and 12 feet high.

From the thickener the thick ferric hydroxide underflow passes to a stainless steel agitating tank, 8 feet in diameter and 8 feet high. It is filtered in a vacuum candle filter consisting of 15 cloth bags, 4 inches in diameter and 41 inches in length. After a water wash, recovered cake, containing some uranium is fed back to the main Pachuca leaching tanks for redissolution. Washings join the filtrate from the candle filter, and the combined solution is added to the thickener overflow in the surge tank.

Uranium is now precipitated from this solution. From the surge tank, the solution passes through a series of three 5- × 5-foot cylindrical agitating tanks. Ammonia gas is supplied from standard storage tanks through a vaporizer until pH 7.0 is reached. At this point, uranium precipitates as a rich yellow ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$.

The uranium precipitate is collected in a thickener (25-foot diameter by 12 feet high) from which it passes to a 8- × 8-foot cylindrical stainless steel agitating tank equipped with steam coils. The thick precipitate is removed by a candle filter composed of 25 cloth bags of the same size used in filtering the iron. These operate under vacuum of 20 to 21 inches of mercury. After washing, the final product of ammonium diuranate contains about 65% moisture and to minimize health hazards, is sent in this form by road tanker to Calcined Products, Ltd., a central calcined works, where it is dried, extruded in pellet form, and calcined to U_3O_8 .

For conversion to uranium oxide, U_3O_8 , the dried ammonium diuranate is heated to 650° to 900° C. The overall reaction is represented by:



Temperature range is important as below 650° C., varying amounts of UO_3 are present and above 900° C., there is oxygen loss from the desired oxide.

After sampling, the extruded pellets, black in color, are packed in steel drums for overseas shipment and subsequent conversion to uranium metal.

The washings and filtrate from the

candle filter and the overflow from the thickener are brought up to nitrate strength by addition of nitric acid. Occasionally, ammonium nitrate or nitric acid and ammonia may be added to adjust nitrate strength. The adjusted solution is recycled to ion exchange columns for re-use.

Recovery of Manganese

Approximately 18,000 tons of manganese ore (40% MnO_2) are required monthly by the South African uranium industry for the oxidant in leaching process. At present pyrolusite ore is obtained cheaply from local deposits. As a protection against depletion of pyrolusite reserves, most of the uranium plants include manganese recovery facilities, which may be used if necessary.

Recovery involves removing the iron, aluminum, and silica, present as hydrated oxides, and precipitating the manganese from the separated solution (Figure 5). Daggafontein's plant is equipped for manganese recovery with 75% recovery efficiency. Effluent from ion exchange columns has following average composition:

	Grams/Liter
Fe^{+++}	3.0
Fe^{++}	4.0
Mn^{++}	6.0
Al	6.0
Free acid	3-4
Total sulfate	35

At present time, this plant is used to



Pyrite content of uranium plant effluent is concentrated in flotation plant and then converted to sulfuric acid. Daggafontein produces sufficient acid for its own use and other uranium plants

neutralize the barren solution. Effluent passes from a steady head tank to a bank of three 10- × 10-foot cylindrical agitators in series; here, pH is adjusted to 9 by addition of lime slurry. Precipitated iron and manganese hydroxide are pumped to a slime dam.

When manganese is being recovered, the ion exchange column effluent passes to the same agitating tanks, where pH is adjusted first to 4.5 by addition of lime slurry. Precipitated iron is concentrated in a 50- × 12-foot thickener, filtered by one of two 14- × 16-foot rotary vacuum filters, and cake is con-

veyed to waste dam. The clear thickener overflow, together with the filtrate from iron separation, are agitated in a 15- × 45-foot nonacid Pachuca and then pumped to a second and similar series of agitating vessels which are non-acid in construction. The pH is raised to 9 with lime slurry. Precipitated $\text{Mn}(\text{OH})_2$ is air agitated in two 22½- × 45-foot nonacid Panchucas in series. In the Panchucas, the $\text{Mn}(\text{OH})_2$ is converted to manganous manganite, $\text{MnO} \cdot \text{MnO}_2$ —i.e., Mn_2O_3 .

The slurry from the agitators is settled in a 50- × 12-foot thickener,

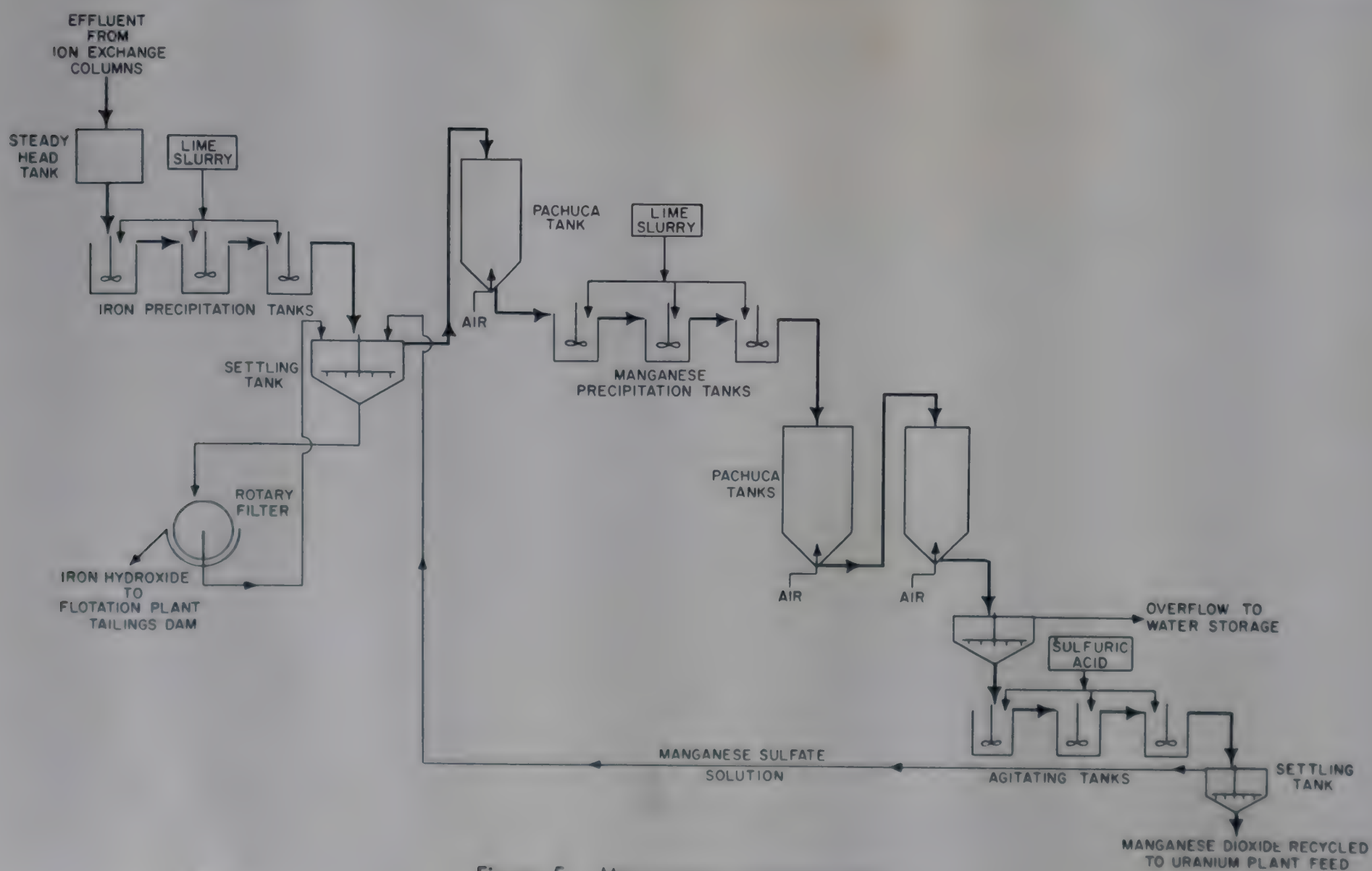


Figure 5. Manganese recovery system

overflow from which is pumped to return water reservoir. Thickened underflow is pumped to a third series of three acidproof agitating tanks, where concentrated sulfuric acid (8 to 20 pounds per 100 pounds of solid Mn_2O_3), is added. The manganous-manganite is converted into insoluble manganese dioxide and soluble manganese sulfate. After being settled, recovered MnO_2 is recycled to uranium plant feed. The manganese sulfate solution is returned to iron separation thickener.

Concentration by Flotation

Most sulfuric acid used in the uranium industry is made from iron pyrites present in the residual pulp of uranium plants. Additional acid is made from pyrites recovered from gold tailings from nonuranium producers. The pyrites content in the original ore is about 5%, and it is necessary to concentrate this prior to conversion in the sulfuric acid plant.

Daggafontein's production of pyrite is 225 tons per day, of which 200 tons go directly to the acid plant and 25 tons to the stock pile. The pyrites is present in the final tertiary filter cake from the uranium plant (Figure 2), which contains approximately 5.0% FeS_2 . This is pumped to a 50- \times 12-foot acid-resisting stock tank where lime is added to adjust pH to 5.7 (5 tons per day). Then it is circulated through a steady head tank and gravitated to three conditioning tanks in parallel, which, by means of launders, feed three banks of 12 rougher cells each (one bank of 10 cleaner cells, and a final bank of 5 recleaner cells). All cells are square units of the Fagergren type equipped with rubber-covered stators and rotors. Rougher cells are 66 inches in size and cleaner and recleaner units 56 inches.

In the flotation plant, the following agents are added at the points indicated and in amounts shown:

Reagent Added	Point of Addition	Amount Added, Lb./Ton Solids
Xanthate 301 ^a	Conditioning tank	0.10
Pine oil	Conditioning tank	0.022
Xanthate 301 ^a	Rougher cell, 9th	0.01-0.03
Depressant 620 ^a	Recleaner cell, 1st	0.09

^a American Cyanamid Co.

Flow through the flotation plant is shown in Figure 2. Final clean concentrates from the recleaner cells, containing 40% sulfur representing 5% by weight of the original feed, are pumped to one of two thickeners, 50 and 60 feet in diameter, where the specific gravity is built up to 1.8 to 1.9.

Thickened pyrites is pumped to 20-

\times 10-foot agitator tanks, from which it is transferred to the primary slurry tank in the acid plant, or is filtered by a 14- \times 16-foot nonacid rotary vacuum filter and cake transferred by conveyor belt to stock pile.

Tailing residue from the flotation plant is adjusted to pH 7.5 by addition of lime and pumped through a 2200-foot column to waste dam.

Sulfuric Acid Production

The sulfuric acid plant at Daggafontein employs the conventional contact process using pyrite as raw material (9). However, it is unique in several respects. Chief difference is that pyrite concentrate is roasted in slurry form in a fluosolids-type reactor rather than as a dry solid. The uranium industry is the first application of the slurry roasting process to sulfuric acid production.

The plant has a rated production of 220 tons of 100% acid per day. Flow is conventional with certain modifications.

Final slurry feed has a solids content of about 67% (specific gravity, 2.0). It is fed into three Fluosolids roasters by single air injectors. Feed rate to each roaster is about 100 tons of slurry every 24 hours. Low-pressure turbo-blowers (5 pounds per square inch gage) driven by 200-hp. motors, supply 3200 cubic feet of air per minute to each roaster. Water sprays maintain roaster bed temperature at 1400° to 1500° F.

Sulfur dioxide gas, excess air, water vapor, nitrogen, and particles from calcined concentrates compose the roaster discharge. This is passed through a stainless steel cyclone which removes approximately 65% of solids, which, together with calcined grate discharge from roaster, are treated for gold recovery.

Gas is then passed through two mild steel cooling and scrubbing towers in series. These are lead and chemical brick lined and packed (approximately 50% of volume) with 6-inch ceramic spiral rings. Flow is upward in each tower. In the second tower, fresh water sprays are counter current to gas flow at three levels. In the first tower, effluent from the second feeds sprays at three corresponding levels. Dissolved sulfur dioxide in the wash water (effluent from the first tower) is removed in a stripping tower and effluent, containing calcines, gravitates to effluent disposal pumps.

Gas from the second quench tower contains some acid mist and minute quantities of dust and is saturated with water vapor. The mist and dust are removed by two parallel electrostatic mist precipitators operating at 62,000 to 65,000 volts (direct current).

At Daggafontein's acid plant, there is only one drying tower rather than the

usual three. It is constructed of mild steel, is 16 feet in diameter and 42 feet high, and is lined with chemical brick. Both 1½- and 3-inch spiral ceramic rings are used as packing. Sulfuric acid (93%) is circulated through the gas entering the tower from the mist precipitators and removes the final trace of moisture.

The dry, cool gas from the drying tower is too concentrated for efficient conversion to sulfur trioxide and eventually into sulfuric acid. Air is drawn into the mixture at the drying tower by the main blower, which is located between the drying tower and heat exchangers. The blower has an inlet capacity of 26,000 cubic feet per minute and is driven by a 600-hp., 1480-r.p.m. motor. The air-gas mixture is forced through three heat exchangers the final of which it leaves at a temperature of 820° F.

From the heat exchangers, the sulfur dioxide-air mixture passes through primary and secondary converters in series. In the converters, vanadium pentoxide catalyst, supported on cast iron grids, converts sulfur dioxide to sulfur trioxide, which is then passed to a single absorption tower where it is absorbed in 98% sulfuric acid circulating through the tower.

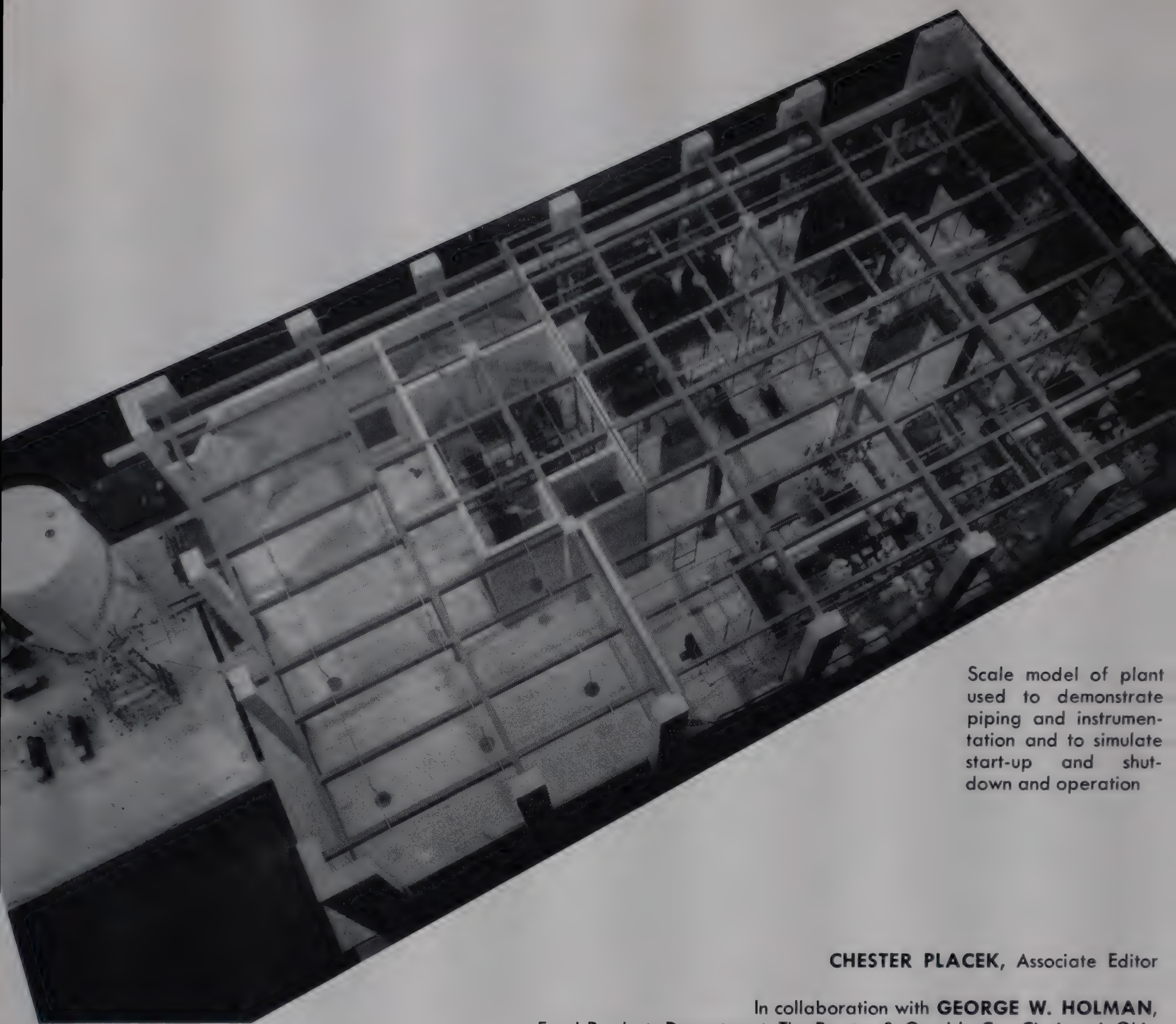
Temperature of 98% acid from the absorption tower is reduced to 200° F. in water-sprayed acid coolers and returned to circulating acid tank. Product acid is bled off from the circulating acid to the absorption tower and pumped to 1000-ton storage tanks.

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Scale model of plant used to demonstrate piping and instrumentation and to simulate start-up and shut-down and operation

CHESTER PLACEK, Associate Editor

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Food Products Department, The Procter & Gamble Co., Cincinnati, Ohio

Directed Interesterification of Lard

LARD—the deposed king of shortening is again coming into its own. After about 30 years of being pushed back by hydrogenated vegetable oils as the “quality” shortening in the consumer’s mind, a lard shortening has made a notable comeback. As a matter of fact, Fluffo, Procter & Gamble’s directly interesterified lard, is second in sales only to P&G’s all vegetable shortening, Crisco, the country’s largest selling shortening today. And this, in only slightly more than 1½ years of consumer availability.

Commercially, lard is the most im-

portant triglyceride material obtained from an animal source. It is usually obtained by heat, solvent extraction, or enzyme treatment of fatty tissue. The most common method of obtaining lard is the so-called wet—or steam—rendering treatment. In this method, fat is separated from tissue by means of hot water or by steam. The hot water process (or low-temperature wet rendering) is conducted at temperatures up to the boiling point of water in open kettles. High-temperature or steam rendering is carried out under pressure in closed vessels. Lard resulting from the

wet rendering process is called prime steam lard. In the dry rendering process, heat alone is used. Dry rendering also includes kettle rendering, in which fat is melted in a hot water or steam-jacketed kettle. Solvent and enzyme treatment are currently not commercially important (10).

Lard’s price fell, relative to vegetable shortening, for several reasons. When compared to good hydrogenated vegetable shortening, “natural” lard has the following disadvantages:

1. Poor oxidative stability, which

creates off-flavor problems in storage and during high temperature use

2. A grainy, translucent appearance and texture that is unattractive when compared to the smooth, white appearance of vegetable shortenings

3. A poor plastic range—too soft at warm temperatures, and too hard when cold. Plastic fats give bread, for example, a high volume because in some way they inhibit diffusion of gas through the dough (3)

4. Nonuniform consistency and flavor which varies with the hog growing season and area, and with the rendering method.

Lard also suffers from poorer creaming ability when compared with hydrogenated shortening. Creaming ability is the measure of the amount of air that can be incorporated into a batter during mixing. The greater the amount of air, the greater is the leavening effect of the shortening.

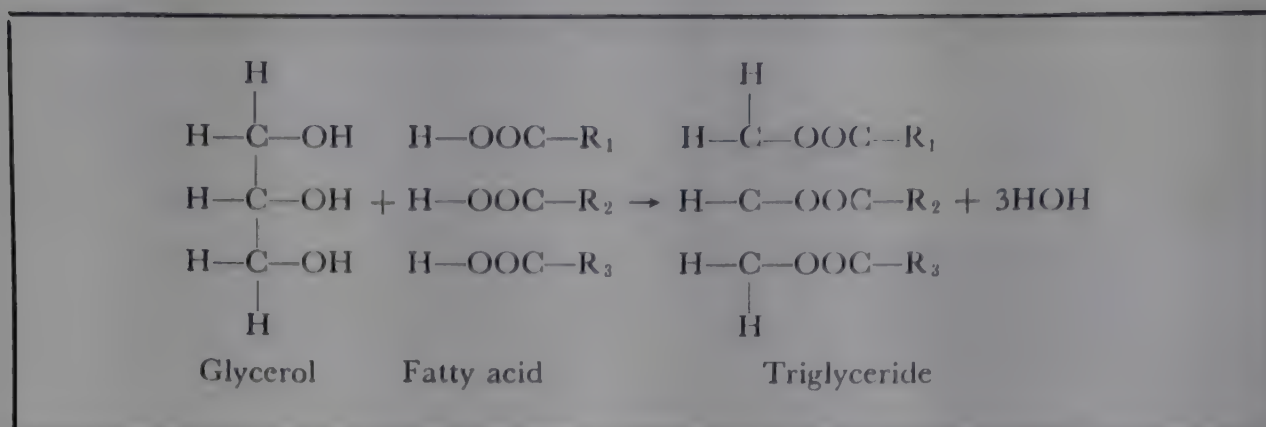
Graininess—natural lard's most undesirable feature—is due to the peculiar crystallizing habits of lard's solid glycerides. These glycerides tend to crystallize into crystals larger than those in typical vegetable shortenings. In addition, the crystals grow during storage and cause extreme graininess by the time the product is marketed. Although most crystals in shortening are too small to be resolved under the microscope, crystal size and shape are the basic factors in graininess.

Economic pressure forced research in methods for overcoming consumer reluctance to lard shortening. Considerable improvement in oxidative stability has been attained through the use of approved antioxidants (9, 13). Hydrogenation, as well as treatment with antioxidants, has made lard equal to vegetable shortenings in frying performance. And graininess started to fall by the wayside with the onset of interesterification processes.

Chemistry of Interesterification

Lard, as well as most fats and oils, consists mainly of triglycerides—glyceryl esters of fatty acids (7). Structurally, a triglyceride is formed by the condensation of one molecule of glycerol with three molecules of fatty acids. The reaction yields three water molecules and one triglyceride molecule.

Consistency of lard as a plastic material is influenced by the size and shape of the solid triglycerides, by their total volume (2) in relation to the liquid triglycerides, and by their polymorphism—different crystal shape and size. In commercial preparation of lard, the fat is usually chilled very rapidly so that crystals are as small as possible. Production of fine crystals extends the product's plastic range and gives it a smooth appearance.



But during storage, graininess occurs when the glyceride crystals grow.

The process of random interesterification (4) can cure the graininess problem in lard, and has been used commercially for the past few years. In randomization, the fatty acids of lard regroup as new triglycerides according to the laws of chance—in a random manner.

Random rearrangement produces its results by breaking up the specific glycerides responsible for the crystal habit of lard. Natural lard's grains are thought to be nearly pure crystals of disaturated glycerides—in natural lard, mostly UPS (unsaturated, palmitic, stearic) (17). Typical lard contains:

Acids	%
Palmitic	27
Stearic	10
Unsaturated or liquid	63 ^a

^a Acids of 51% oleic, 11% linoleic, 0.6% linolenic, and 0.4% arachidonic.

Random interesterification is achieved by heating lard for 0.5 to 6 hours at 50° to 260° C. in the presence of a suitable catalyst. Most commercial randomization is currently carried out at about 60° C. for 30 minutes with sodium methylate.

But even after randomization, the plastic-range problem is not fully resolved (8). The disaturated glycerides in randomized lard give little plasticity at higher temperatures. Therefore, 9 to 12% of completely hydrogenated fat (usually cottonseed oil or lard flakes) is added to the randomized fat. This imparts sufficient body, or plasticity, at warm temperatures.

But in addition to being relatively more costly, the addition of the hydrogenated vegetable fat in some formulations creates the problem of the shortening now being too firm at cold temperatures. This hardness at temperatures below room temperature also limits the amount of subsequent hydrogenation that can be used with the lard itself.

Directed interesterification is a solution to this problem of plastic range (6, 10). In directed interesterification, the reaction is carried on just below the melting point of the fat. The high melting fractions (trisaturated glycerides) are made to precipitate, and interesterification takes place in the remaining liquid phase. This forces the equilib-

rium toward the direction of formation of more trisaturated glycerides which, in turn, also precipitate. Precipitation of the trisaturates leaves additional liquid material, and interesterification continues.

The directed interesterification process, developed by Eckey of P&G (5, 6), is far more versatile than random rearrangement. By conducting rearrangement and simultaneously removing from the sphere of reaction (by crystallization) the trisaturated glycerides that are formed, it is possible to concentrate the saturated acids of a fat largely into a trisaturated glyceride fraction.

The segregation of saturated acids into trisaturated glycerides is accompanied by a corresponding tendency for unsaturated acids to form triunsaturated glycerides. This breaks up the mixed saturated-unsaturated acid glycerides which are prominent in all natural fats. Since the presence of such mixed glycerides contributes to sharp melting and to a short plastic range, "unmixing" gives the reverse—gradual melting and a long plastic range (4). Thus, body characteristics are improved by directed interesterification (4, 8). The trick in the process is to carry out the ester interchange at such low temperatures that simultaneous crystallization of glycerides will bring about the desired results.

During experimental work on interesterification, sodium methylate was used as a catalyst because of its low cost, stability, and ease of preparation. However, other sodium or potassium alcoholates are also effective, as well as the metals themselves. For random rearrangement, the same alcoholates can be used as well as the broad group of aromatic or aliphatic-aromatic sulfonic acids, metals such as cadmium, lead, tin, zinc, and their compounds, and compounds of the alkali metals or of the alkaline earth metals. Currently, sodium methoxide is used almost exclusively for randomization processes because of availability and ease of handling. The other catalysts, although effective, pose price and toxicity problems.

For its directed rearrangement process, P&G uses sodium-potassium alloy catalyst. The high activity of sodium-potassium enables the use of considerably lower temperatures (7) for interesterification than with either metal

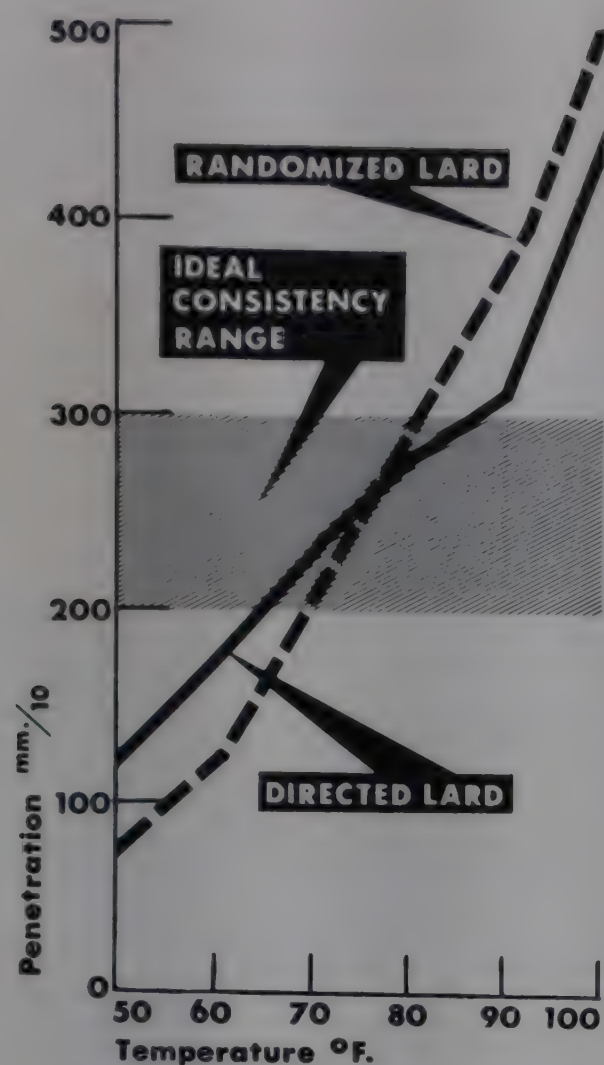


Figure 1. Directed and randomized lard in plastic range

alone or with the alcoholates. Greater activity of sodium-potassium over a catalyst such as sodium itself can probably be partially explained by its liquid properties. Catalyst particles in fat probably become coated with oxide because of the reaction with traces of oxygen and peroxides occurring in fat. The action of solid sodium particles, for example, is partially blocked by this oxide coating. With the alloy, the liquid sodium-potassium particles seem to keep unreacted metal on the surface. An observation that lends weight to this theory is that small particles of sodium-potassium will catch fire in air due to rapid oxidation. Similar sodium particles usually oxidize on the surface only. In addition to its high activity, sodium-potassium has the advantage of being well-suited to continuous metering.

As the fraction containing trisaturated glycerides is increased by directed interesterification, the disaturated and monosaturated glycerides fraction decreases.

Studies (8) of directly interesterified lard show that:

- ▶ Trisaturated glycerides formed by this reaction eliminate the need for the addition of completely hydrogenated vegetable fat (hardstock).
- ▶ The decrease in disaturated glycerides means less total solid glycerides at cold temperatures—about 50° F.—than are present in a natural or randomized lard to which the customary 10% hardstock has been added.

▶ If no hardstock is added, a better control of hydrogenation can be obtained for any given hardness or penetration level than could be performed on randomized lard to which hardstock has been added.

▶ Because the disaturates are reduced by about 25 to 30%, UPS (unsaturated, palmitic, stearic) remaining after interesterification will be correspondingly reduced, causing a greater resistance to graining of disaturated glycerides than is possible in randomized lard (8).

The difference between directed and randomized lard shortenings is in plastic range (8), depending on formulation. In Figure 1, for example, both shortenings were prepared from the same base lard and hydrogenated to about the same extent. The randomized lard had 9.5% of completely hydrogenated cottonseed oil added, while no hardstock was added to the directed lard. The latter shows that it is softer below 70° F. than randomized lard, and firmer above 70° F. As a measure, plastic range can be expressed as the number of degrees enclosed between the arbitrary limits of 200 and 300 penetration—the middle of the penetration range.

In baking performance, directly interesterified lard has all the desirable properties of vegetable shortening. The directed lard is stable against change under market-aging conditions.

Development of Process

Initial laboratory and pilot plant work for directed rearrangement of lard at P&G was done by the batch method. Sodium methoxide or metallic sodium was mixed into melted and previously dried fat. The mass of fat was gradually cooled by setting the batch at successively lower temperatures by circulating cooling water through coils or through a jacket. Slow agitation was used to assist heat transfer. When trisaturated glycerides begin to crystallize, the mass has a sharp increase in viscosity. Heat transfer becomes poor and agitation is difficult. Several days are required for the reaction to reach the desired quantity of trisaturated glycerides.

Factory application of such a batch process would have proved clumsy, difficult to control, and expensive because of slow reaction time involving large amounts of in-process lard. A continuous process was the only practical answer.

This early development work showed that the factors that control or limit the rate of directed interesterification are:

1. Rate of interesterification in the liquid phase; or randomization
2. Rate of heat removal
3. Extent of nucleation—number of

crystal centers formed on which trisaturates can crystallize

4. Rate at which trisaturates crystallize out of the liquid phase

Random interesterification rates are important since the trisaturates can only precipitate as rapidly as they are formed in the liquid phase (8). This rate can be somewhat rapid when an active catalyst such as sodium-potassium is used. With 0.20% sodium metal, random equilibrium is reached in about 20 to 30 minutes at 140° F. But using sodium-potassium alloy with the same sodium equivalent, random equilibrium is reached in 6 minutes at 120° F.

Heat removal from fat, especially from a mixture of solid and liquid fat, is difficult because of fat's poor conductivity and the relatively low convection obtained in such a viscous or plastic medium. The heat to be removed totals about 28 B.t.u. for each pound of fat. P&G found that efficient high heat removal rates are obtained by using commercial shortening heat exchange (Votator) units. Heat transfer rates of about 250 B.t.u./hr./sq. ft./°F. are obtained with the equipment.

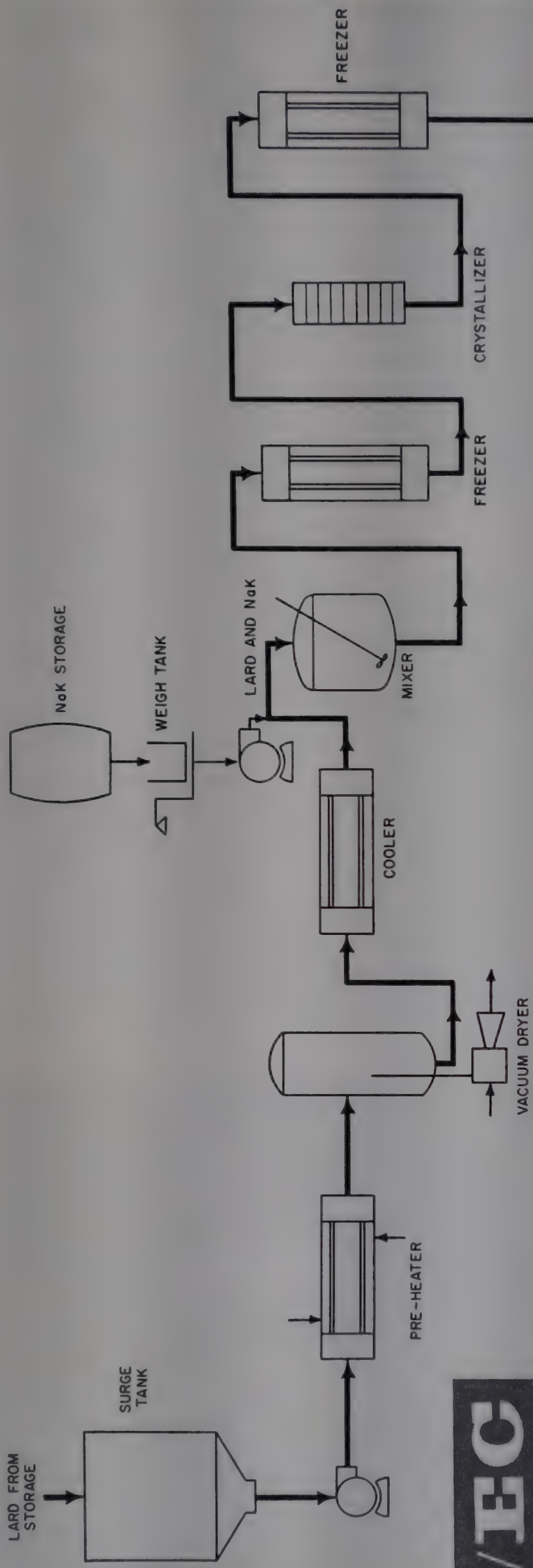
Many nuclei are also formed with the chilling equipment because the fat is cooled rapidly (in 15 seconds) to a temperature far below its melting point. The rapid chilling quickly develops a fine cloud which consists of many more nuclei than could be obtained with a slow chilling process.

A remaining problem, which is probably the limiting factor in the process as it now stands, is the crystallization of the trisaturated molecules. The crystallization of trisaturates is a diffusional process which is hindered by the viscous nature of the lard at this stage. Agitation is a great help in speeding crystallization. Optimum agitation is a gentle but a thorough movement throughout the crystallizing mass. Not enough agitation results in partial solidification of the crystallizing lard, and too much results in an excessive heat input.

An interesting departure during plant construction was the building of a model for simulating actual plant start-up and shut-down, and operation. A number of problems concerning instrumentation, safety, ease of operation, and process control arose in designing the plant. The model of the plant used in resolving these problems included piping and instrumentation. Concerning safety, the model helped to visualize every circumstance where a failure of an instrument, a control, or a pump would cause a hazardous situation to arise.

Factory Application

As finally developed, the continuous directed interesterification process at P&G's Ivorydale (Cincinnati) plant



I/EC

PLANT PROCESS SERIES

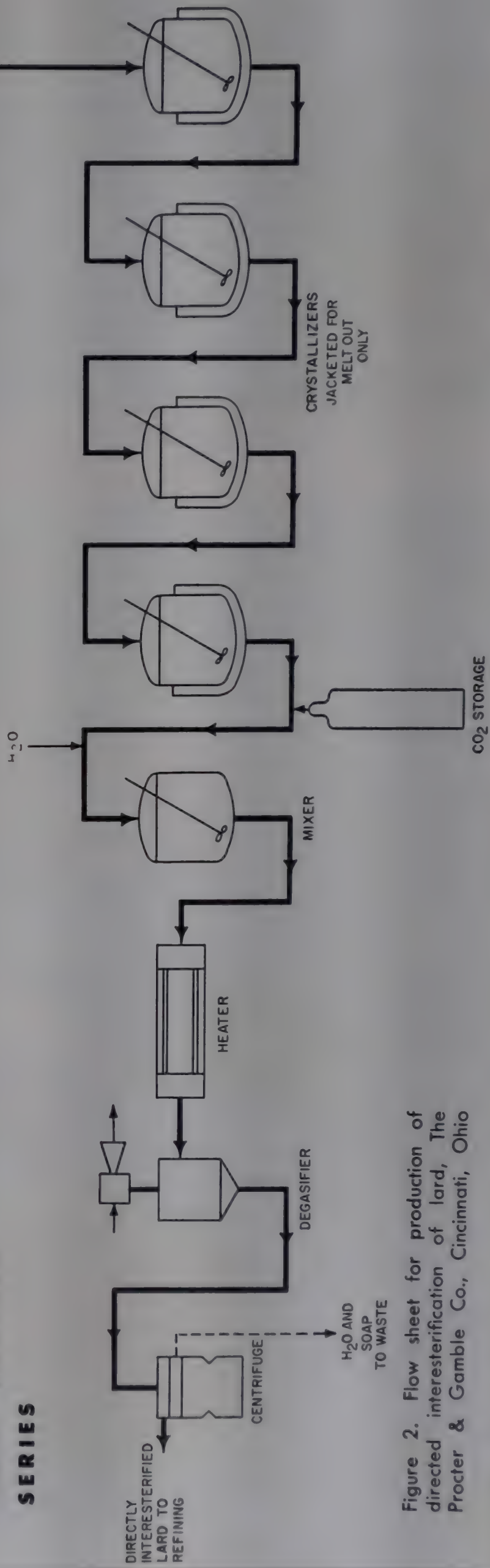
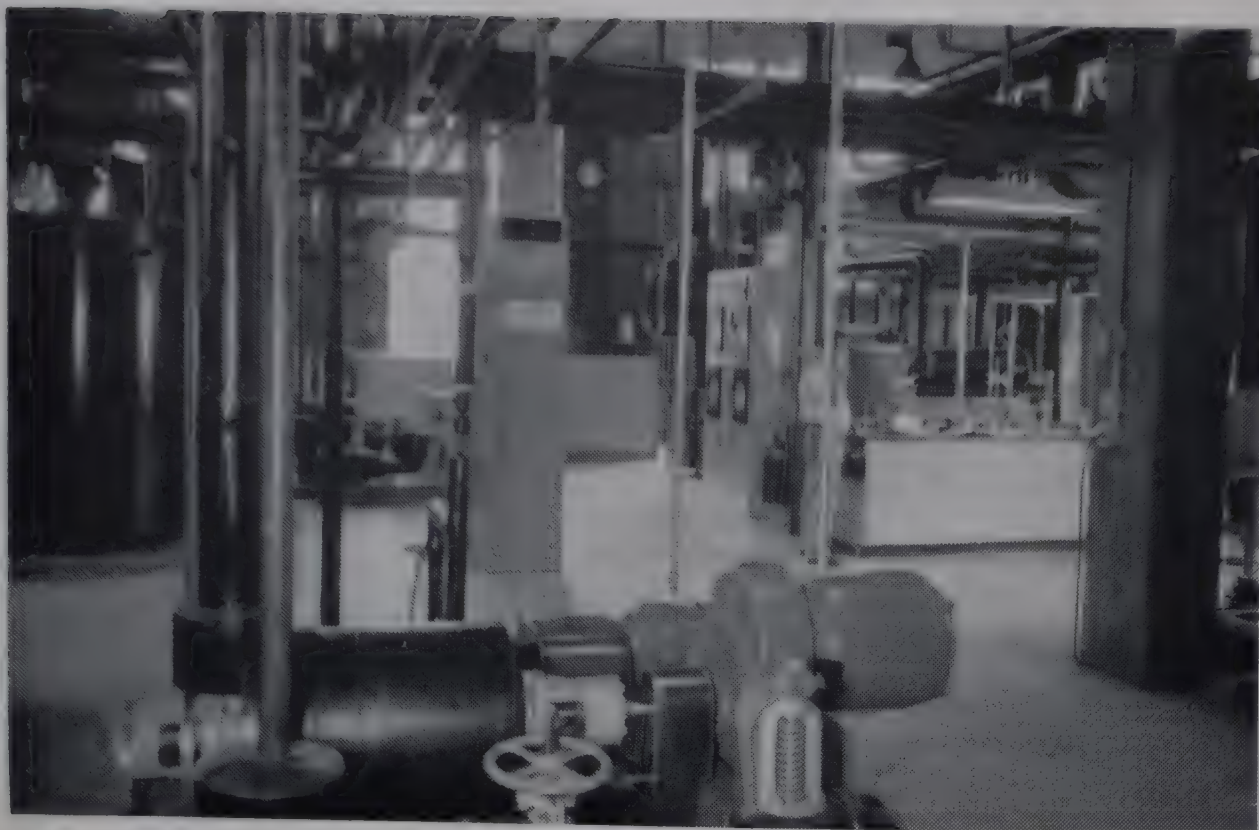


Figure 2. Flow sheet for production of directly interesterified lard, The Procter & Gamble Co., Cincinnati, Ohio



Operating area at Ivorydale plant

Left, crystallizers. Right, Votators. Front, neutralizing mixer

consists of mixing melted lard with finely dispersed catalyst, and inducing the crystallization of trisaturated glycerides by rapid cooling. Initial heat of crystallization is removed by pumping the mixture through a heat exchanger, from where the product enters a series of crystallizing tanks. The reaction is completed in the crystallizers, each tank carrying the reaction a step nearer to completion. After leaving the last crystallizer, catalyst is removed and the rearranged lard is sent to further refining.

Fat refining—bleaching, hydrogenation, and deodorization—have been described previously in this series (12). Antioxidants and monoglycerides are

added after deodorization. Carotene, 10 to 15 p.p.m. apparent β -carotene, is added to the product after refining to impart the characteristic golden color to Fluffo.

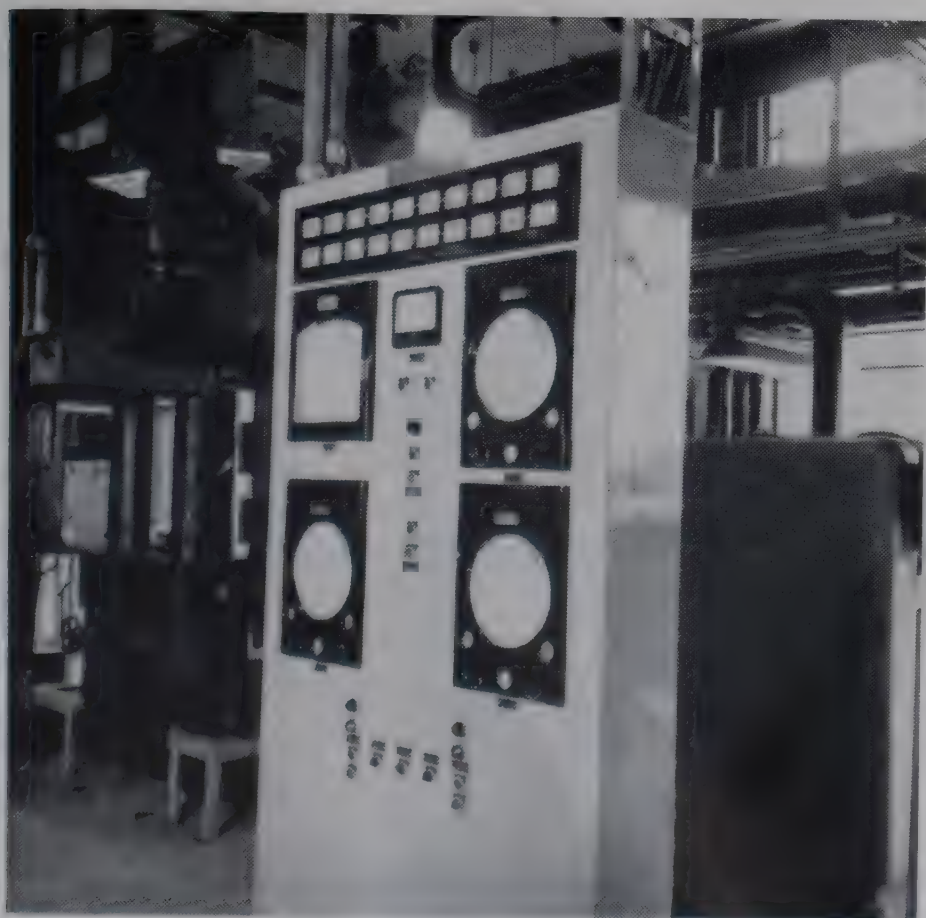
Lard arrives at the P&G plant in tank cars, and is stored in steel tanks in several locations. In Figure 2, the lard enters the process stream from a steel surge tank (7E) which has a capacity of about 200,000 pounds. The lard is pumped into a preheater (8E) and then through a P&G designed dryer (18E) followed by cooling to a temperature just above its melting point by passage through a heat exchanger (5E). A carefully metered (14E) stream of cat-

alyst is pumped with the lard into a small mixer (11E, 16E) in which the sodium-potassium is suspended throughout the lard as particles of 10 to 40 microns in diameter.

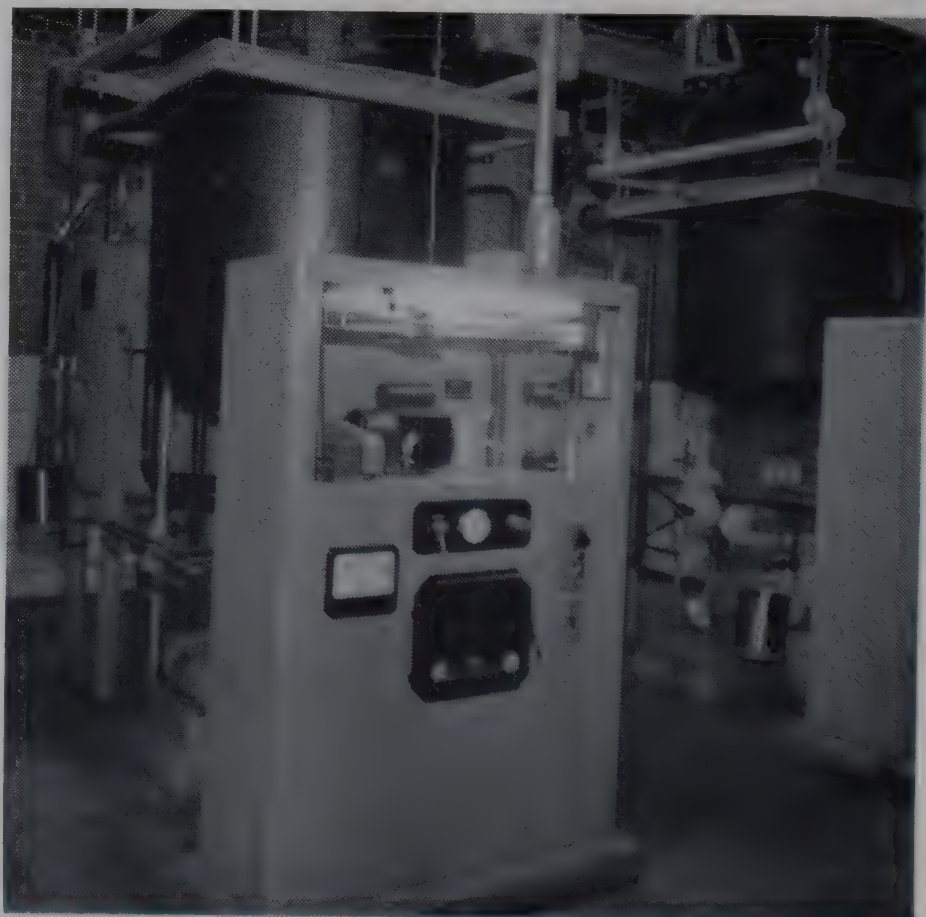
Generally, the sodium-potassium ratio in the catalyst is 1 to 1, although many other combinations serve satisfactorily (7). The limiting factor is that the alloy's melting point should be no higher than 120° F. Catalyst concentration for the rearrangement is 0.10 to 0.20%, with an excess of about 0.02% to remove free fatty acids, peroxides, and moisture present in the lard.

The catalyst-oil mixer is an enclosed mixing device having a relatively small barrel-shaped rotor cage mounted on a vertical axis. On small units, the cage is driven at 15,000 r.p.m., while on large units, 3600 r.p.m. is the optimum speed.

The metering principle used for sodium-potassium is based upon a variable speed positive displacement pump of a special design to prevent valve blockage. Speed, and therefore output, of the pump is controlled electrically by the speed of a traveling poise on the sodium-potassium scale tank which is part of the alloy metering system. A main control panel (2E) in the operating area controls the speed of the traveling poise and the speed of the pump. The entire sodium-potassium metering system is interlocked with oil flow. If the oil flow stops, the system cannot be filled with catalyst. Once the alloy is suitably dispersed in the lard, it is safe and constitutes no particular hazard other than a small evolution of hydrogen which is vented. All pumps (12E, 19E) are



Main control panel in the center of room monitors and controls automated plant



Sodium-potassium system and feed tanks

positive displacement-type pumps driven (4E) through eddy current clutches, enabling pump speed to be electrically remote controlled.

Plant operation, once begun, is monitored and controlled from the centralized control panel. The panel houses motor starters, the catalyst metering system controls, temperature controls for the entire system, oil flow controls, and an alarm system.

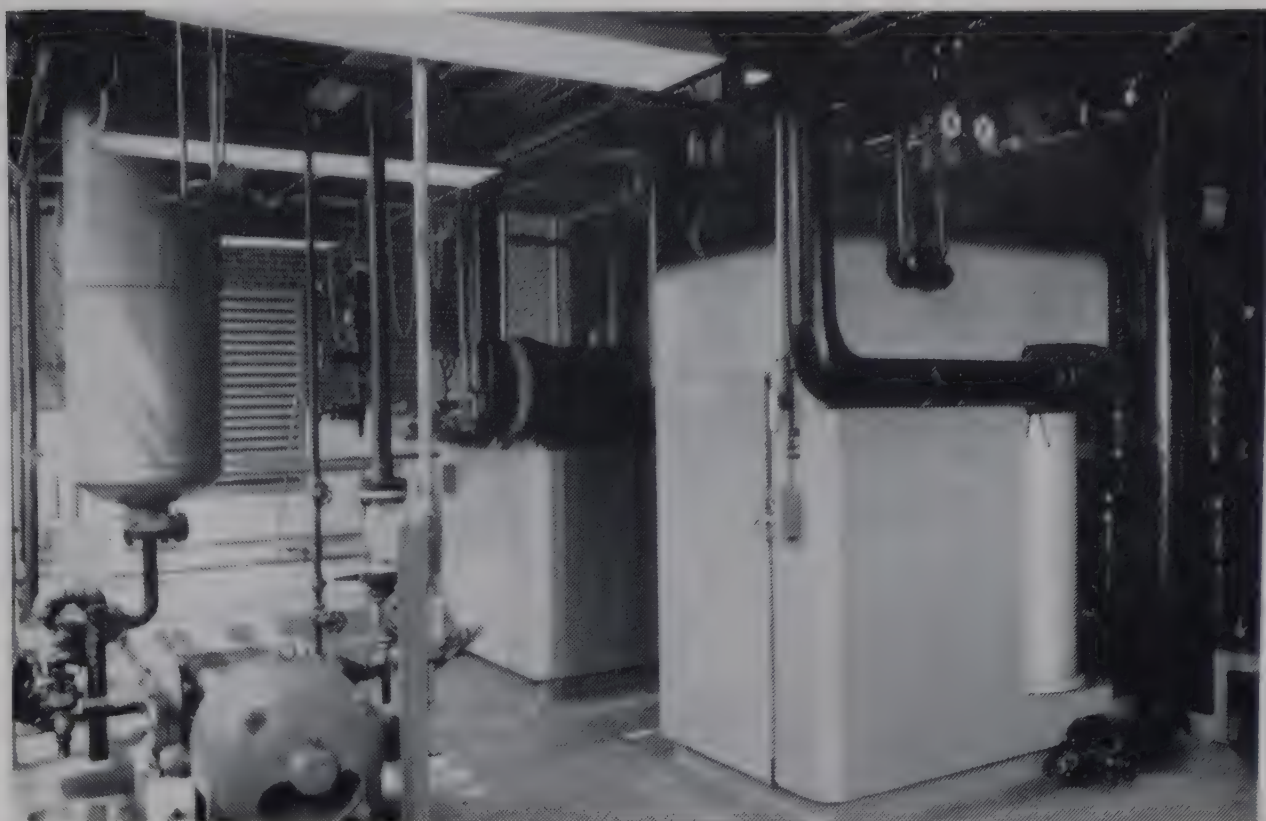
A short incubation period is required before sodium-potassium becomes active. The lag before the onset of the reaction may be due to the reaction between catalyst and lard impurities (7). From the alloy-lard mixer, the catalyzed substance flows through a brine-cooled, scraped-wall heat exchanger (5E) in which the temperature is quickly dropped to the point necessary for starting crystallization of trisaturated glycerides, about 70° to 75° F. One freezing unit (Votator) has a capacity of 10,000 pounds of lard per hour, and is chilled with direct expansion ammonia (20E). Since a freeze-up in this equipment can shut down the plant for several hours, the ammonia system is equipped with automatic controls (10E, 21E) which dump the ammonia if the lard temperature falls below a predetermined point.

From the heat exchanger, the stock goes to an agitated first stage crystallizer (6E). In here, the directed interesterification begins.

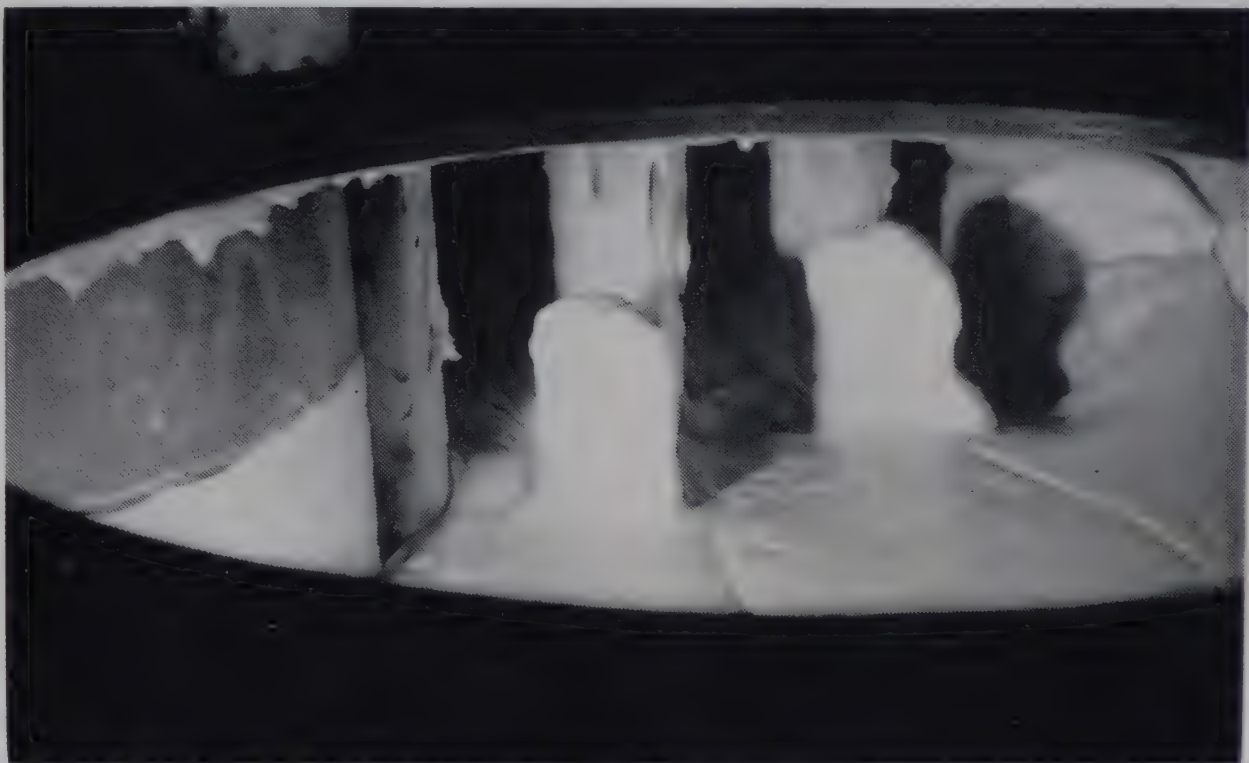
In this stage, two things are occurring at the same time. First, any trisaturated glycerides present begin to crystallize; second, interesterification in the liquid phase forms more trisaturated glycerides in an attempt to restore the equilibrium distribution. This first crystallizing stage liberates considerable heat. Since the temperature rises beyond the desired range, a second cooling set-up is required to bring the stock to below its crystallizing temperature. This is accomplished again with another Votator unit.

After the second cooling, the lard is pumped to a battery of four P&G designed mild steel constructed crystallizers (15E). The second crystallization stage takes much longer to allow completion of the reaction. Crystallization slows down after the initial driving force diminishes.

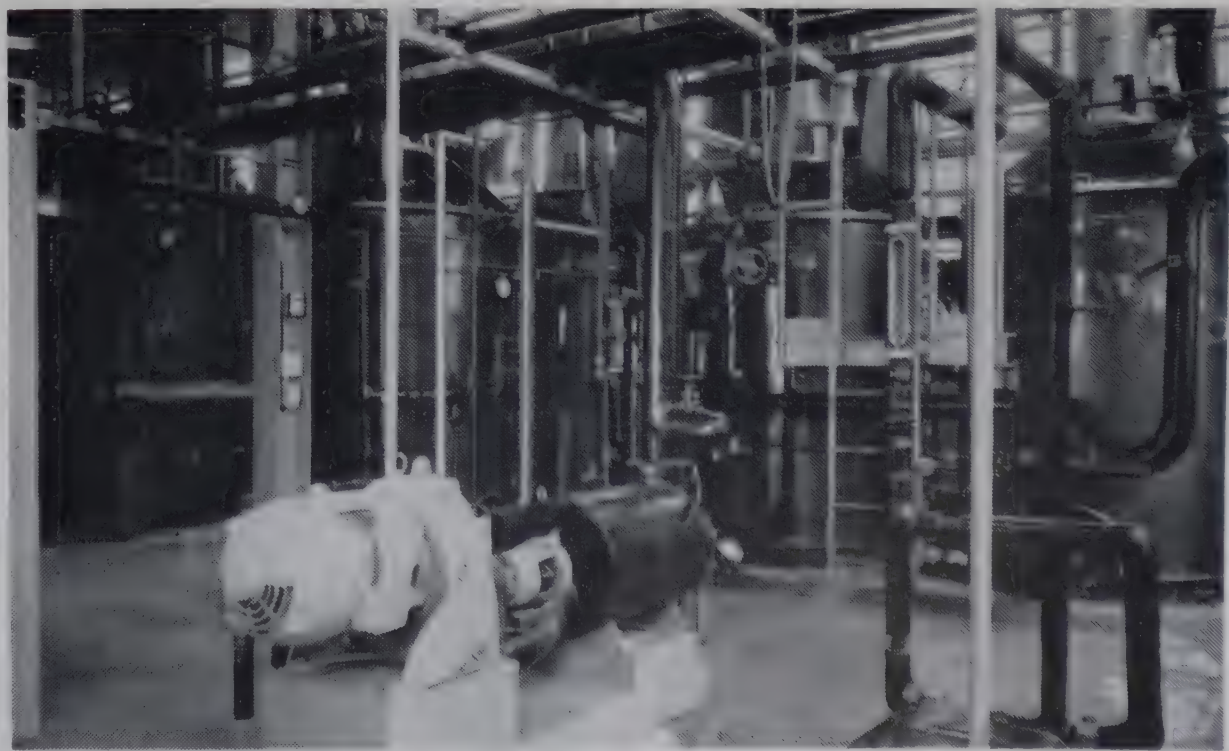
Considerable study was made in designing these crystallizers, in which the most critical part of the process takes place. Actually, each crystallizer contains a separate stage of crystallization, and each is a separately agitated vessel with a capacity of about 5700 pounds of lard. To avoid pressure vessels, which would be necessary if the system were held hydraulically full, the crystallizers are built so that the lard overflows by gravity through the four tanks. Agitation in the crystallizers consists of moving vertical pitched blades which intermesh with vertical pitched stator



Votator units used to chill the reaction mixture rapidly



Inside a crystallizer, lard undergoes one stage of directed interesterification



Four crystallizing tanks, each with capacity of 5700 pounds of lard (background), where second stage of crystallization takes place. Foreground. Product flows into neutralizer mixer from last tank



Plant operator performs cloud point test, most critical control, on P&G designed unit (right)

blades. The outside blade moves very close to the vessel wall, keeping it nearly free of solidified lard. The stator blade cleans the central drive shaft. The careful agitation is necessary because the crystallizing lard must be kept in gentle motion throughout its mass. In this way, the lard is very fluid, but will set up hard in any unagitated spot or on any surface that is not scraped. Crystallizing time is controlled through bypassing one or more vessels and/or varying the level in the last crystallizer.

Lard temperature rises throughout crystallizing because of the heat of crystallization of the trisaturates. The stock emerges from the crystallizers at 90° to 100° F., depending on the concentration of trisaturated glycerides.

As the interesterified fat leaves the last crystallizer, it flows into a company designed, high-speed neutralizer mixer (17E), in which water (9E) and carbon dioxide—which is kept in outside storage tanks—are added to kill the catalyst. If the catalyst is not killed when crystallization stops and before melting the lard, the reaction reverses itself. Carbon dioxide is added to counteract the alkalinity of the resulting sodium and potassium hydroxides.

From the neutralizer mixer, the rearranged lard is pumped into a degasifier (13E) after being warmed in another preheater. The degasifier is designed in the same way as a vacuum dryer, but is operated at higher pressures (15 to 20 mm. of mercury) and lower temperatures. Only the hydrogen and

carbon dioxide are stripped in the degasifier, and essentially no water is removed.

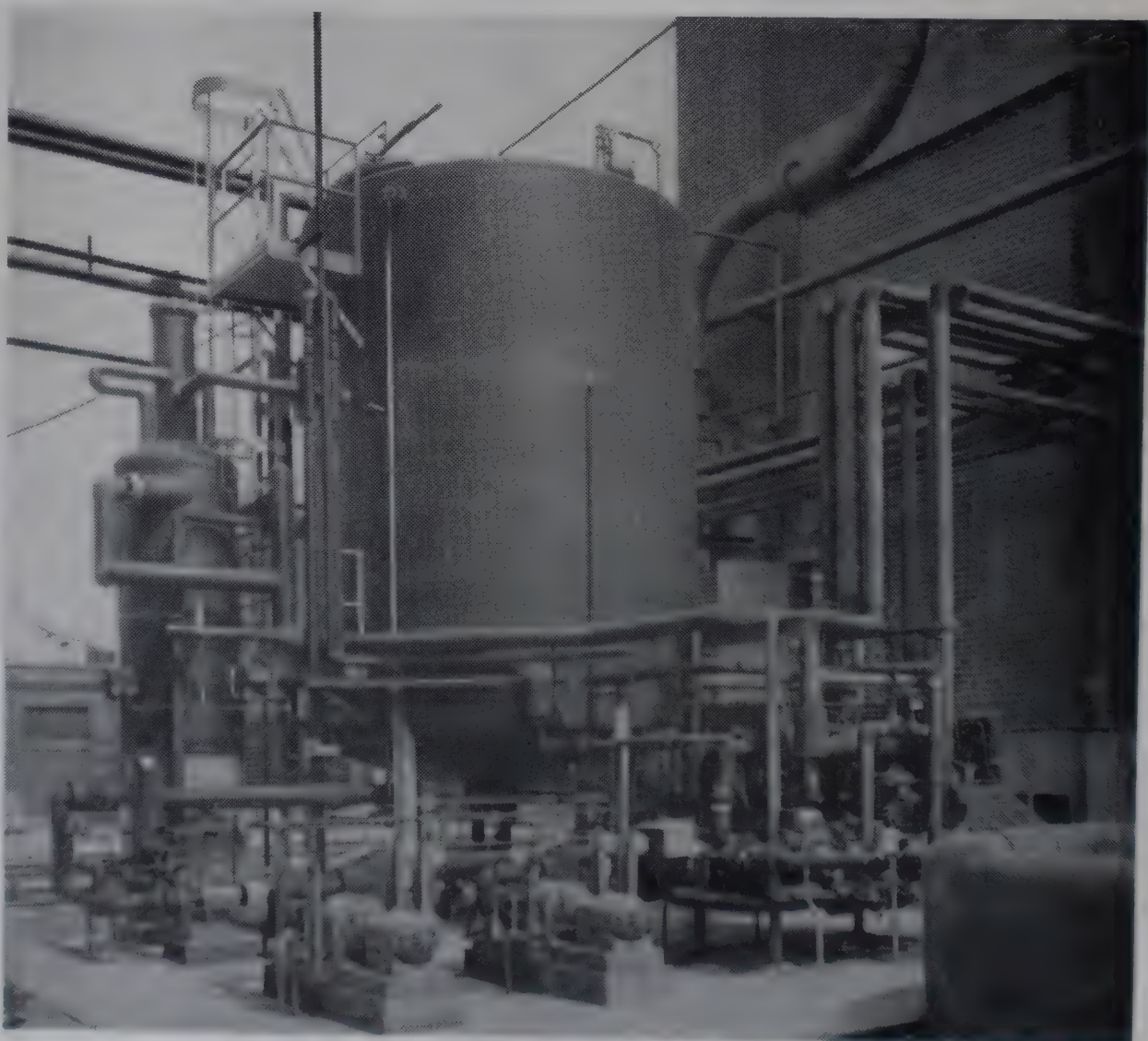
A little soap is formed in the sodium-potassium "killing" step due to initial

free fatty acids in the lard. The soap is removed by continuous oil refining centrifuges (1E, 3E) that have a capacity of 5000 pounds of interesterified lard per hour. The residual soaps are further removed by conventional water washing and additional centrifuging. Fatty acids are recovered from the soap stock and are used in the manufacture of soap products. The interesterified lard is then dried in a continuous vacuum dryer (18E) and then goes on to final processing.

Operating Technology Control and Safety

The completely automated, one-man operated directed interesterification plant represents a capital investment of about \$500,000. Directly interesterified lard is made continuously 24 hours a day and 5 days a week. The normal work week begins at midnight on Sunday and ends at midnight the following Friday.

In the start-up stage, lard is first introduced into the system. After a few minutes, sodium-potassium catalyst flow is started. Until operating conditions (equilibrium) are reached, material appearing at the end of the run is usually not interesterified to the desired point and is recycled after catalyst separation. For shutdown, catalyst flow is stopped first. Refrigeration is then discontinued to enable melting out of the system, the stream is diverted to a holding



Surge tank outside plant. Left, degasifier



Catalyst is stored in separate room with sloping floor for drainage

tank, and is then recycled to the starting tank for the next run. Melting out takes approximately 3 to 4 hours.

Cloud point is the most critical control test used, since it indicates the extent of interesterification. A company designed instrument is capable of making direct cloud point readings on a fat sample. The procedure varies somewhat from the cloud point tester previously described

(12). A sample of interesterified fat is warmed to 60° C. and placed in an electrolytic-type beaker (Corning No. 1140). A flowing stream of water—temperature 7° C. or less—is passed around the beaker containing the agitated sample. Temperature of the sample drops from 60° to 40° C. in about 1 minute. A white light beam is passed through the sample. The beam is of sufficient intensity so that a photocell registers 2 μ a. when the sample is all liquid. For this test, the cloud point is the temperature at which intensity of the beam is reduced to 31.4% of the initial intensity.

Other control measures include the usual color and free fatty acid determinations after the centrifuging and vacuum drying steps. The final control test for trisaturated triglyceride content is the solid content index (SCI) at 92° F.

The sodium-potassium drum storage area contains most of the hazards associated with the plant. In addition, unloading of the drums into the scale tank and metering sodium-potassium into the lard stream are additional danger points. No steam or water lines are found in the alloy storage area. A sloping floor permits drainage to the center of the room in case of leakage or spills. The drums are unloaded by nitrogen pressure in a separate cubicle. In here, the operator can apply or release nitrogen pressure from outside the area. Scale tanks and metering pumps are adjacent to the sodium-potassium storage area and are enclosed by tile walls.

P&G has a similar plant operating in Dallas, Tex.

Some interesterified lard goes into bulk shortening for bakery and hotel use. An all-purpose shortening, adjusted to a different consistency, is called Pertex. A directed lard shortening for cakes containing monoglycerides is known as Selex.

New Process Developments

Several improvements in the process have been achieved since the plant first went on stream during the early part of 1955. Catalyst usage was recently reduced by about 30 to 40% from its initial 0.25%. Soap formation represents a dead loss. Attempts are being made to reduce this formation, which is now at a very low level—about 1 to 2%.

Experimental work with tallow is currently being investigated. Successful commercial runs have been made using tallow to replace part of the lard. In some cases, all the lard was replaced by tallow. Since fatty acid composition of tallow differs widely from that of lard, P&G has developed special techniques to attain the same finished product quality.

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Processing Equipment

- (1E) Allis-Chalmers Manufacturing Co., Milwaukee 1, Wis., continuous centrifugal pumps.
- (2E) Continental Electric Co., Inc., Newark 5, N. Y., central control panel.
- (3E) De Laval Separator Co., Poughkeepsie, N. Y., continuous oil refining centrifuges.
- (4E) Eaton Manufacturing Co., Dynamatic Division, Kenosha, Wis., drives for positive displacement pumps.
- (5E) Girdler Co., Votator Division, division of National Cylinder Gas Co., Louisville 1, Ky., Votator—standard shortening heat exchanger.
- (6E) *Ibid.*, Votator B unit (picker box).
- (7E) Harris, A. M., Inc., Cincinnati, Ohio, surge tank.
- (8E) Kewanee-Ross Corp., Buffalo, N. Y., preheaters and coolers.
- (9E) Milton Roy Co., Philadelphia 18, Pa., water metering pump for neutralizing catalyst.
- (10E) Minneapolis-Honeywell Regulator Co., Minneapolis 8, Minn., ammonia automatic controls.
- (11E) Nooter Corp., St. Louis 4, Mo., tank for catalyst-oil mixer.
- (12E) Northern Ordnance, Inc., Minneapolis, Minn., positive displacement pumps.
- (13E) Ohio Machine and Boiler Co., Cleveland, Ohio, degasifier.
- (14E) Omega Machine Co., Division of B-I-F-Industries, Inc., Providence, R. I., sodium-potassium metering system.
- (15E) Patterson Foundry and Machine Co., East Liverpool, Ohio, crystallizers.
- (16E) Premier Mill Corp., Geneva, N. Y., agitator for catalyst-oil mixer.
- (17E) Steel Products Engineering Co., Springfield, Ohio, neutralizer mixer.
- (18E) Whitlock Manufacturing Co., Hartford 10, Conn., vacuum dryer.
- (19E) Worthington Corp., Harrison, N. J., positive displacement pumps.
- (20E) York Corp., York, Pa., ammonia compressors.
- (21E) *Ibid.*, ammonia automatic controls.



Sodium-potassium drums are unloaded by nitrogen pressure from separate cubicle

Boron Chemicals from Searles Lake Brines

GORDON H. BIXLER, Associate Editor

in collaboration with

DWIGHT L. SAWYER

American Potash & Chemical Corp., Trona, Calif.

NOSE about among market development men these days, ask what's hot, and chances are better than good you'll find they dip into inorganic chemistry to come up with an answer. Reason: Today's inorganic chemist has dusted off his prosaic starting materials, dashed to bits his classical ideas about simple molecules and reactions, and found he can manhandle some inorganic atoms much like his heretofore more glamorous brothers in organic chemistry.

Not all elements of the periodic table dazzle the imagination, but there's enough new in the inorganic chemistry of several to keep a galaxy of research and market men intrigued for some time. Among these newcomers—the chemistry of boron.

Inorganic boron compounds have been around for a long time. Boron's magnetism today stems from totally new uses or potential uses—as a fuel or fuel additive, in heat-stable polymers, in shields for atomic reactors, in solar batteries, and as borate esters for a raft of applications.

Boron's story starts with some form of boric oxide deposit, for boron doesn't occur free in nature. A number of countries have minor deposits, among

them Italy, where boric acid is obtained from volcanic emissions. The United States has a corner on recoverable boron reserves, with some 95% of the world's supply centered in southern California's desert regions.

California sources are of two types—sodium tetraborate decahydrate or borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in brines of “dry” lake beds; and underground deposits of kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) mixed with borax. Boron chemicals have come from several different California locations in the past, but only two deposits are important commercially now—the brines of Searles Lake and the underground deposits at Boron, Calif., 60 miles away.

Three major borax producers operate today—U. S. Borax & Chemical Corp., Pacific Coast Borax Co. Division, at Boron, Calif., on a below-ground deposit; and American Potash & Chemical Corp. at Trona and West End Chemical Co. at Westend on Searles Lake. Of these three, American Potash is second in size, making 25% of U. S. basic boron chemicals; Pacific Coast Borax makes 70% and West End 5%. At one time, Columbia-Southern Chemical Corp. recovered a small amount of

borax from brines of nearby Owens Lake as a minor coproduct from sodium carbonate and bicarbonate production, but no longer does so. Owens Lake brine contains some 3,800,000 tons of sodium borate, but development there has lagged well behind that at Searles Lake where the deposit is much more extensive. History and geology of Owens Lake has been covered by Dub (1).

The Searles Lake and Boron, Calif., deposits are different, one a multicomponent brine, the other relatively simple sodium borate minerals. Processing has accordingly been different at the two locations. To take Pacific Coast Borax (PCB) first, its history and that of its predecessors date from the late 1800's when Death Valley was the major U. S. borax source. (From this period, incidentally, comes the now familiar trade-mark, 20 Mule Team Borax.) In 1925, PCB found the kernite deposit at Boron, and since 1928 all its ore production was centered there.

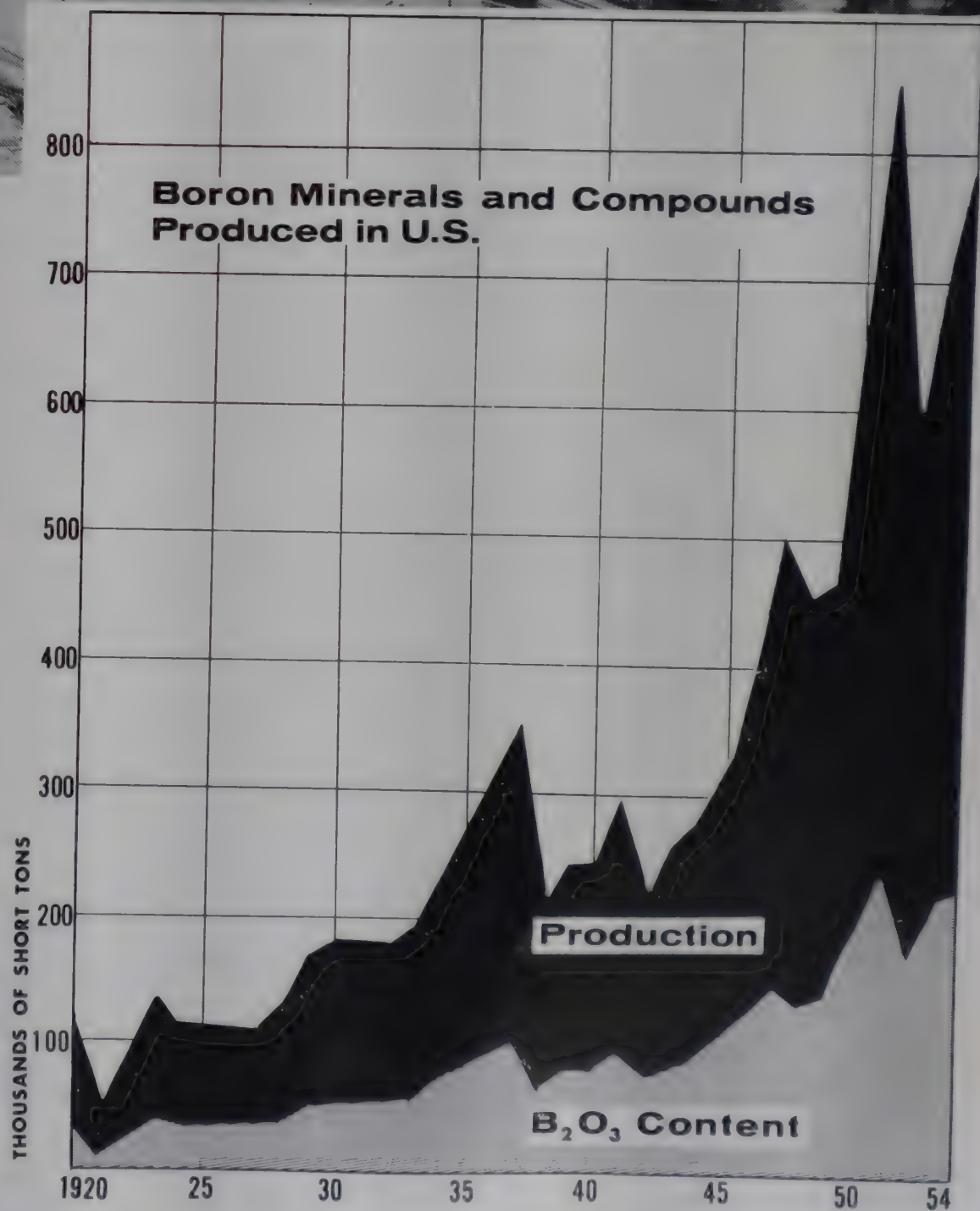
The kernite deposit lies under some 400 to 500 feet of overburden and has been mined by usual underground methods. Some of the ore is partly concentrated at the mine site. PCB sells



the concentrate, mostly in foreign markets, for processing into refined borax and boric acid. The balance of the ore is shipped to the company's refinery at Wilmington, Calif., where various refined products are made, including borax, anhydrous borax, and boric acid.

PCB is putting finishing touches to an \$18,000,000 expansion and modernization program. Part of the tab is for shifting from underground to open-pit mining, but a large portion is for a new concentrating plant and a new refinery at Boron to replace existing units. At the new refinery expected to start in the second half of this year, PCB will open-pit mine borax ore, dissolve it in recycling refinery end liquor, remove part of the insoluble shale in gigantic thickeners, and filter the resulting borax solution. Borax will then be crystallized from this solution as sodium tetraborate decahydrate or pentahydrate by controlling temperature in vacuum crystallizers. Dried borax will serve as feed material for further processing to boric acid and anhydrous borax.

The third producer, West End Chemical, uses carbonation on Searles Lake brines in a process similar to American



SOURCE: CHEMICAL ECONOMICS HANDBOOK, STANDARD RESEARCH INST

Table I. Chronology at Searles Lake^a

Date	Product	Remarks
1873	Borax	Borax Lake Mining District ^b organized with borax recovered by leaching surface scrapings
1878	Borax	John W. Searles formed San Bernardino Borax Mining Co. Process was leaching surface scrapings followed by simple crystallizing
1895		SBBM sold to Pacific Coast Borax, which closed plant and concentrated on Death Valley deposits
1908	Soda ash	California Trona Co. formed to recover Na ₂ CO ₃ from brines and solid reefs. Company never got started, went into receivership in 1909
1912		American Trona Co. takes over California Trona assets
1914	Potash, borax, sodium sulfate	Original American Trona plant completed but failed to operate properly and was abandoned
1916	Potash	American Trona Co. process for getting potash from brines pans out and continuous production begins at present Trona, Calif., site
1916	Potash	Pacific Coast Borax and Solvay Process start a joint operation at Borosolvay. Plant closed 1920
1919	Borax	Added to American Trona product line
1926		American Trona merged into American Potash & Chemical Corp.
1927	Boric acid	Both technical and U.S.P. grades produced
1934	Sodium carbonate, sodium sulfate	New plant section built to recover these
1935	Anhydrous borax	First of a series of upgradings of a basic product into a more "concentrated" form
1936	Potassium sulfate	Produced from KCl, burkeite (2Na ₂ SO ₄ ·Na ₂ CO ₃), or sodium sulfate
1938	Lithium concentrate (LiNaPO ₄)	Prior to recovery, this was an annoying impurity that scaled heat transfer surfaces
1940	Chemical grade KCl, bromine	Bromine extracted from agricultural grade KCl to make chemical grade KCl
1946	Borax, sodium carbonate	\$6,000,000 plant addition finished to process lower structure brines and boost basic capacity
1951	Lithium carbonate	Upgrading of crude lithium concentrate
1951	Phosphoric acid	By-product of Li ₂ CO ₃ plant

^a All products and processes those of American Potash except where noted.

^b Not to be confused with Borax Lake, Lake County, Calif., where several hundred tons of tincal crystals were recovered from mud about 1870.

Potash's, where carbon dioxide precipitates sodium bicarbonate. This is filtered off, calcined, and recrystallized as sodium carbonate. Borax is recovered from the filtrate by cooling. West End also recovers sodium sulfate.

History of Searles Lake, its formation and "phase rule" recovery of chemicals from its brines, has been dealt with by many writers, including Teeple (2).

Briefly, therefore, Searles Lake covers 34 square miles, about 12 of which is exposed salt bed in the center (mud washed down from surrounding hills covers lake edges). The bed actually consists of two separate salt structures, an upper one 70 to 90 feet thick and a lower one 25 to 40 feet thick. An impervious mud parting layer 13 feet thick divides the two.

Both salt structures are porous (40 to 50% voids) and filled completely with a concentrated brine. Upper structure brine is rich in potash, while the lower structure is rich in carbonate and borate

Chemical recovery at Searles Lake started in 1873 when the first simple borax works reclaimed solid phase material (Table I). In 1916 chemists succeeded in getting chemicals from the brine itself. The first potash product supplied the critical needs during World War I, and the present American Potash operation at Trona began that year.

American Potash has added to its product line at Trona in two ways—by getting new chemicals from the brines and by upgrading chemicals already produced. A move to anhydrous borax in 1935 typifies the latter. Borax is nearly 50% water, and making an anhydrous form obviously saves shipping costs. A swing from crude lithium concentrate to lithium carbonate in 1951 is another example. As to new chemicals from the brines, the biggest single addition came in 1946 when the company completed a new plant which uses a flue gas carbonation process to recover soda ash and borax from lower lake structure brines.

Since the mid-1940's, American Potash has spent over \$1,000,000 a year to modernize and expand plant facilities. The Trona plant, incidentally, has run since 1916, except for 10 months in 1921 when then owner American Trona revised the plant in light of better phase rule data.

Chemicals from Searles Lake Brines

A so-called "main plant cycle" and a carbonation plant make up the two basic sections at Trona. In the main plant cycle, oldest at Trona, American Potash evaporates and fractionally crystallizes upper structure brine to recover eight primary chemicals in a series of plants in sequence (eight more chemicals stem from the primary ones, to give a total count at Trona of 16). The carbonation plant processes lower structure brine to add to production of two chemicals, sodium carbonate and borax. The two sections are tied together in that the carbonation plant furnishes a crude sodium bicarbonate-borax mixture to the main plant cycle.

American Potash owns 4 square miles in the center of the lake and leases an additional 10. In the upper structure, richest brine lies at the bottom near the parting mud layer, so wells are drilled and cased to within a few feet of the mud layer. Pumps pull brine from each well at 50 gallons a minute. Flow to the main plant cycle is 2200 gallons a minute. Raw brine enters the main plant cycle at the

► **Evaporation Plant.** Here, three triple effect evaporators concentrate 3,100,000 gallons of brine a day to 1,400,000 gallons (equal to 7 tons of water evaporated every minute). Sodium chloride, sodium carbonate, and burkeite (double salt of sodium carbonate and sodium sulfate) crystallize during evaporation and are separated and conveyed off the cycle to the

► **Soda Products Plant.** In this plant, the salts are separated into sodium carbonate, sodium sulfate, and desiccated sodium sulfate. A dilithium sodium phosphate by-product from these steps is further processed in a separate plant to produce lithium carbonate and phosphoric acid. Sodium chloride from

Chemicals from Searles Lake Brines

Primary	Derived
Sodium carbonate	Sodium sulfate, desiccated
Sodium sulfate	Potassium chloride, chemical grade
Lithium carbonate	Borax pentahydrate
Phosphoric acid	Boric acid
Potassium chloride, agricultural grade	Anhydrous borax
Potassium sulfate	Sodium pentaborate
Bromine	
Borax decahydrate	

the evaporators is dissolved in brackish well water and returned to the lake. Meanwhile, in the main plant cycle, the evaporator effluent, which is a concentrated potash-borax liquor, goes to the

► **Potash Crystallization Plant.** Borax crystallizes slowly, so operators cool the solution rapidly to get a crop of potassium chloride crystals and leave a solution supersaturated in borax. Part of the potassium chloride is dried and sold directly as crude, agricultural grade potash, part is converted to potassium sulfate, and the balance is refined to chemical grade potassium chloride. In the latter step, bromine is removed by chlorination and steam stripping. Some of the product is marketed, and the rest is used to make organic bromides at a subsidiary plant. Residual liquor from the potash crystallization plant goes to the

► **Borax Plant.** There, seeding and slow crystallization produce a crude sodium tetraborate pentahydrate. The crude pentahydrate is filtered out, redissolved, and then recrystallized, producing either sodium tetraborate decahydrate (borax) or the pentahydrate. Refined borax serves as feed to the other two borax plant sections—boric acid and anhydrous borax.

Anhydrous borax is made by heating borax to its melting point—about 1370° F.—in large fusion furnaces. This drives off all water of hydration and leaves $\text{Na}_2\text{B}_4\text{O}_7$.

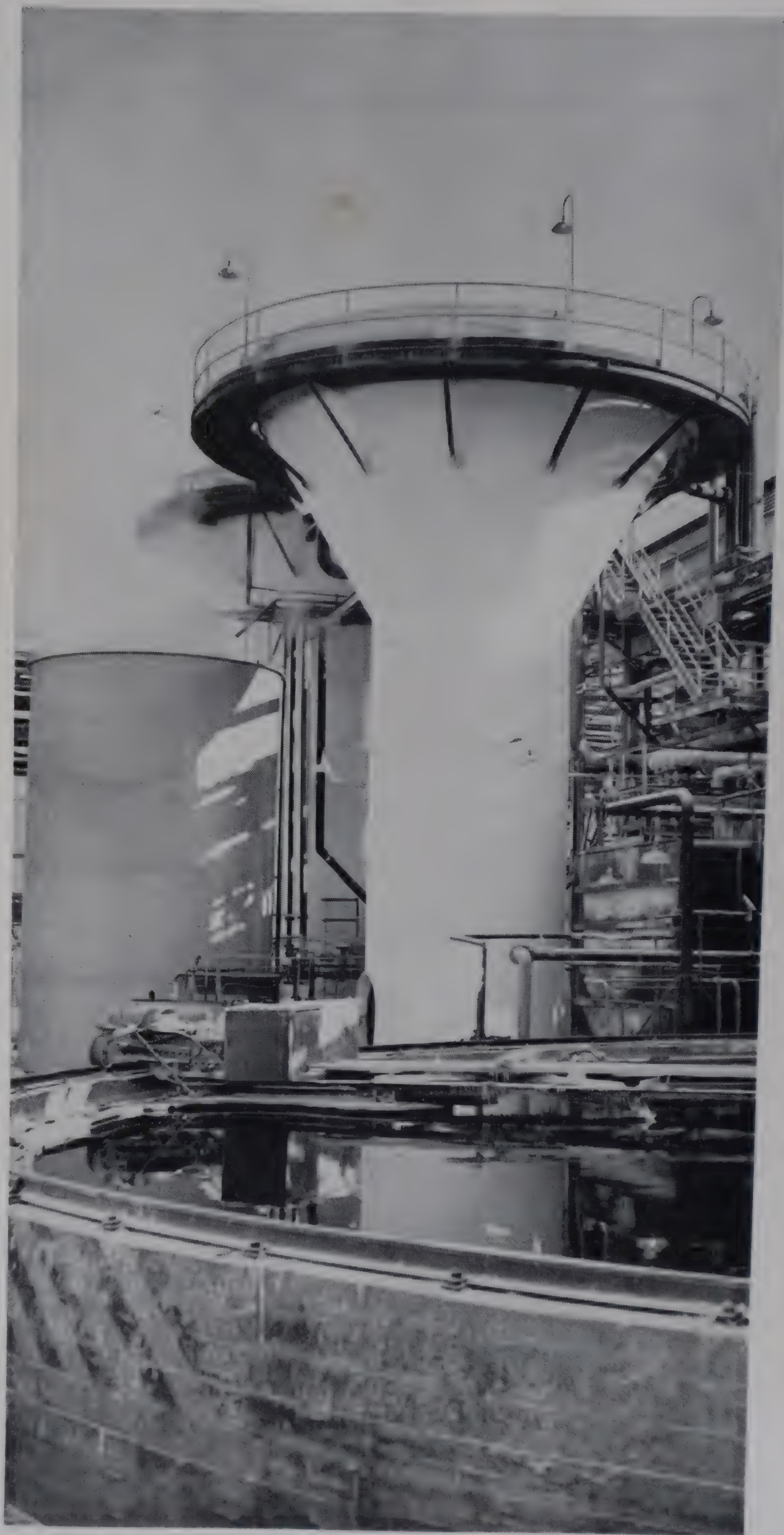
Residual liquor from the borax plant then goes to the evaporation plant where it joins raw brine entering the cycle. This mixture becomes evaporator house feed stock.

At the carbonation plant, carbon dioxide bubbled through lower lake structure brine produces sodium bicarbonate. This is filtered off, calcined, and recrystallized as sodium carbonate monohydrate. The filtrate, rich in borax, is neutralized with uncarbonated lake brine and is then refrigerated to crystallize the borax. The crude borax is separated and goes to the main cycle borax plant for refining, and the filtrate returns to the lake.

Crystallization

The borax plant at Trona consists of two sections—crude borax crystallization, where the crude sodium tetraborate pentahydrate is removed from main plant cycle liquors, and borax refining. In the latter step the crude material is redissolved, crystallized either as the penta- or decahydrate, and dried for storage. Some is sold, and the rest serves as feed for the boric acid and anhydrous borax plants.

The borax process (Figure 1) actu-



First step in the borax plant is recovery of a crop of crude borax crystals in two crystallizers (background). The thickener (foreground) recovers fine crystals washing out in the overflow from the settling cone at the top of crystallizers

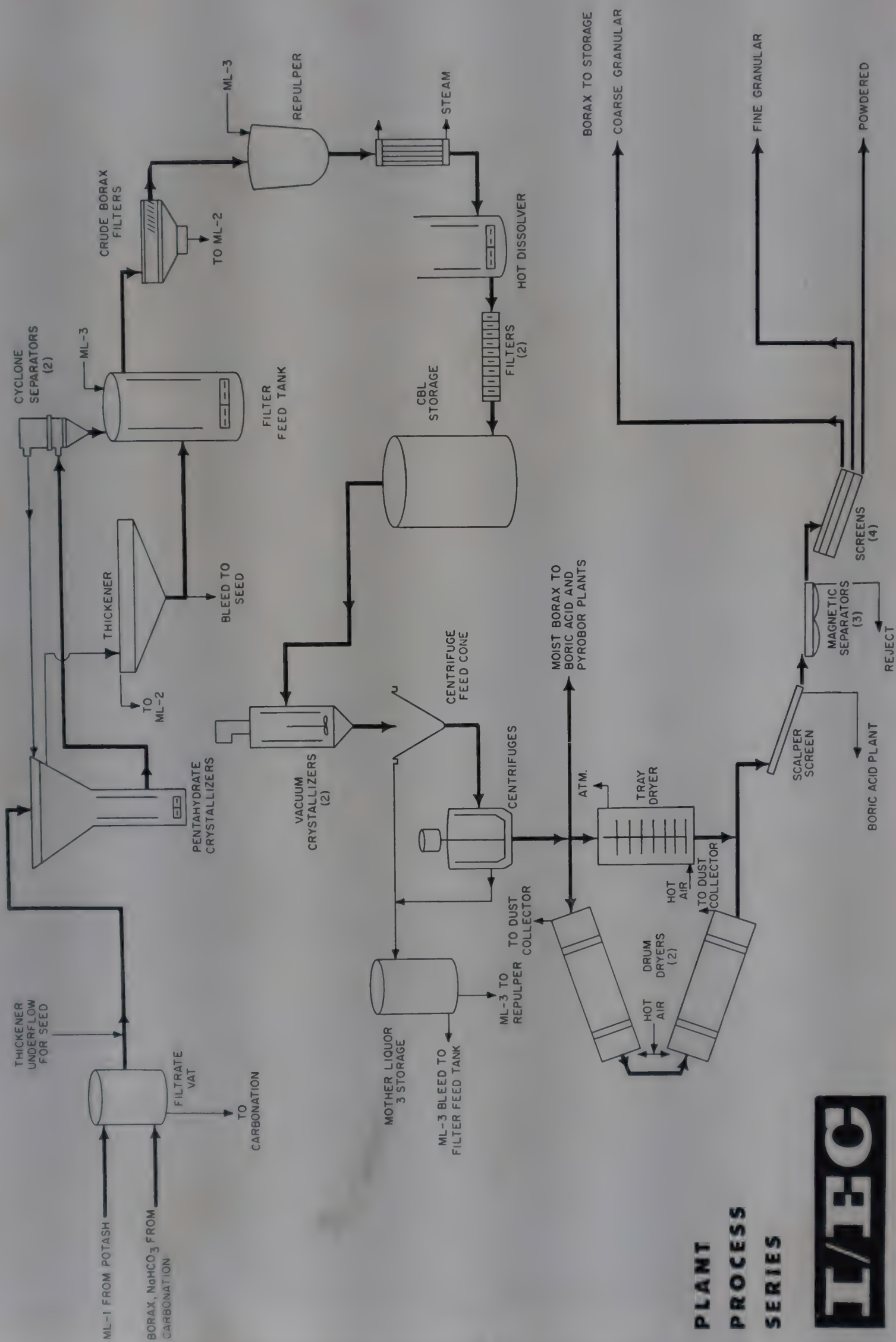
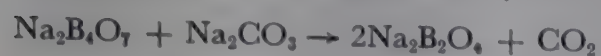


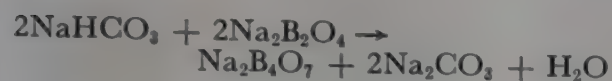
Figure 1. Flowsheet for production of borax from Searles Lake, American Potash & Chemical Corp., Trona, Calif.

ally starts in the potash plant at a large, 50,000-gallon tank, the filtrate vat. This tank serves as a surge tank for residual liquor from the potash plant—mother liquor 1 ("1" means Searles Lake brine has produced its first crop of crystals—potash).

In the evaporation plant, tetraborate reacts slightly with alkaline carbonate to form sodium metaborate during the final high temperatures reached in evaporation on the main plant cycle:



Since metaborate is very soluble in mother liquor-1 (ML-1) and will not crystallize under the same conditions as the tetraborate, it would continue to flow through the plant in cycling liquors, increase the specific gravity of the potash plant feed liquor, reduce the solubility of potassium chloride, and adversely affect other solubility relationships. However, this situation is remedied by the reaction:



A sodium bicarbonate-borax mixture from the carbonation plant provides both sodium bicarbonate for this reaction and additional borax.

In this process, ML-1 is pumped from the filtrate vat to the carbonation plant. There, borax produced by the carbonation plant is slurried in ML-1, bicarbonate added at a rate of 25 to 35 tons a day, and the slurry pumped back to the filtrate vat. Reaction between bicarbonate and metaborate and the conversion of the borax decahydrate to the pentahydrate is rapid and is probably complete by the time ML-1 reaches the borax plant proper.

In addition to being a surge tank and a point of control for metaborate, the filtrate vat also helps to deaerate ML-1. Foaming is most serious in the crude crystallizers, where it causes fine pentahydrate crystals to float over the overflow and recycle to the evaporator unit. To remove air and thus reduce foaming, ML-1 is held for a short period in the filtrate vat before being piped to the borax plant itself. To keep more air from being added, a level controller on the filtrate vat stops drawdown to the point where pumps would "gulp air."

ML-1 feeds to two crude crystallizers, and a crop of sodium tetraborate pentahydrate crystals is precipitated from the supersaturated borax solution by adding seed crystals. The latter are withdrawn from the underflow of the next unit in the flow sequence—a thickener.

The crystallizers are large, agitated tanks with settling cones at the top. Working with both crystallizers is a 60-foot Dorr thickener and two Ameri-

can Potash-designed cyclone separators, one for each crystallizer. To start dewatering crude borax, the crystallizers, cyclones, and thickener work together.

It is desirable to keep a heavy seed bed in the crystallizers to make sure as much borax crystallizes as possible; hence, cone settlers at the top of each crystallizer. Since crystals stay in the crystallizers as long as possible, they grow fairly large—up to about 12 mesh. This means the sludge can be classified economically in cyclone separators before being fed to filters for final dewatering. Sludge is thus drawn from the crystallizer settling cone and fed to a cyclone. The cyclone thickens +60-mesh crystals to 70 to 80% settled solids by volume, and the thickened sludge then flows to the filter feed tank. Liquor and -60-mesh crystals return to the crystallizers.

Meanwhile, excess liquor in the crystallizer flows over the launder at the settling cone lip, carrying very fine pentahydrate crystals with it. Overflows from both crystallizers feed the thickener where these small crude crystals are thickened. Part of the underflow from the thickener is fed to the crystallizers as seed, while the balance goes to the filter feed tank.

Overflow from the crystallizers normally contains 6 to 8% settled solids by volume, and the thickener recovers most of these fine crystals. However, if ML-1 has not been deaerated properly, process efficiency drops as fine crystals float out of the thickener and recycle to the evaporation plant. While not lost, recycling borax means inefficient operation, so good deaeration is a must.

Dewatering of the crude borax slurry takes place in two horizontal, 13-foot flat bed filters, with an older drum filter being held in stand-by reserve.

Filtrate from the dewatering step joins thickener overflow. The combined stream is mother liquor 2 (having produced a second crop of crystals—borax). ML-2 (Table II) is still rich in borax—about 7% and potash 12%—so it is blended with raw brine entering the main plant cycle. The mixture becomes evaporator feed liquor.

Borax in ML-2 also serves as a process check point, with the control range being >7.2 to 7.5%. If borax in ML-2 is over 7.5%, either processing temperatures have been too high, excessive quantities of suspended fine crystalline borax are present, or too much metaborate has formed. If the latter occurs, the plant operators ask that more bicarbonate be slurried in the ML-1 slip stream to the carbonation plant.

Refined Borax

Crude sodium tetraborate pentahy-

In-Process and Control Analyses . . .

Borax Plant

In the crude cycle, slurry samples are taken each hour from the pentahydrate crystallizers, Dorr thickener underflow, filter feed slurry storage tank, and Sharples feed cone underflow stream. Liquor samples of the concentrated borax liquor in the hot dissolver are taken every 2 hours and analyzed for chloride (as potassium chloride) and borax. The pH of refinery crystallizer mother liquor is controlled by adding caustic to the CBL. Every 4 hours, samples of Sharples feed cone overflow are checked with a special amber electrode to maintain a pH range of 9.7 to 10.0. Borax solubility in ML-2 is checked every 2 hours; a range of 7.2 to 7.5 is desired; values above 7.5 indicate that additional bicarbonate is required. To control drying, samples of the Wyssmont and rotary dryer discharge are analyzed every 2 hours for total borax decahydrate; values between 100 and 102% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ are desired. A borax dryer product analyzing 100% has a damp appearance and is difficult to screen. Powdered borax samples are run for chloride control. When specially screened products are analyzed, screen controls provide necessary checks every 2 hours. Special samples for iron control during the pentahydrate run provide a check on the magnetic separators. Two samples per shift are sufficient to control the iron content as Fe_2O_3 to less than 0.0007%.

Process Control

One centrally located control laboratory serves the entire Trona plant. Daily composites are made from regular samples. Analyses are published in a daily laboratory report which is divided into two sections, process samples and finished products. With exception of analyses of the calciner discharge and scrubber liquor in the anhydrous borax plant, no chemical analyses are conducted by operating personnel. Routine analyses of the ditch or effluent liquors from the boric acid and borax plant are made of composited 8-hour samples provided by special automatic sampling devices. Barometric injection and tail water samples from these plants are handled similarly.

Specific samples of anhydrous borax for control purposes are not generally run. Daily composites are checked for borax content, magnetic and total iron, and visible impurities.

Clean-Up and Maintenance

The Trona process is mainly crystallization, and most clean-up is based on removing salt build-ups, either to let equipment work well or to stop contamination products. The Trona process is also largely cyclic, with one section getting "raw materials" from the preceding one and in turn sending end liquors to the following. Thus, regular maintenance and clean-up times in one section depend on those in another. The borax plant coordinates with the potash plant for scheduled clean-up. The anhydrous borax plant does not handle solutions, so its maintenance is primarily mechanical.

The potash plant washout comes three times a week, and the borax plant schedules washouts at the same time. Potash plant washout takes about 4 hours, but borax takes about 6, mainly because the borax refinery sections must be cleaned thoroughly. Because the crude and refined borax processes are independent, neither the potash nor carbonation plants must surge their feeds to borax while borax completes the clean-up program. However, carbonation surges to a borax thickener in its plant during washouts at the potash plant.

Main washout points in the borax plant are crude coolers, crude filters, centrifuge feed cone, concentrated borax liquor filter, vacuum crystallizers, centrifuges, and feed piping systems. Liquor storage tanks—concentrated borax liquor and ML-3—are hardly ever washed out, for high temperatures prevent build-ups at these points. Crude pentahydrate crystallizer washout are scheduled when needed because of build-ups. The thickener is cleaned about every 6 months, a 14-hour job. ML-2 at 200° F. is used to wash crude filters and is then sent to process streams. Hot condensate or filtered "ditch" water is used to wash the centrifuge feed cone, centrifuges, and miscellaneous lines. Hot concentrated borax liquor is used to wash the refinery crystallizers and is then rerouted to process.

The anhydrous borax plant has no regular clean-up schedule for the entire plant, but sections are cleaned as needed.

drate is contaminated with entrained mother liquor and at times with small amounts (0.3 to 0.7%) of potassium chloride which pass through the potash plant filter screens. This crude material is dissolved in a cycling filtrate (ML-3) from the refining process itself to make a concentrated borax liquor (CBL). Refined borax is then obtained from CBL by vacuum crystallizing, followed by dewatering and drying. The material is subsequently screened and stored for shipping. It can also be used for feed to the boric acid and anhydrous sodium tetraborate plants.

Besides the refined borax, American Potash makes a refined sodium tetraborate pentahydrate in the same crystallizing equipment as that used for producing refined borax, depending on sales needs. Special precautions are necessary in producing the pentahydrate, since a drop in temperature below the transition point to the decahydrate causes the cake to "set up." Change-over from penta- to decahydrate runs takes place between normal washout periods in the refinery.

Crude borax from the horizontal, flat-bed filters is conveyed continuously to a repulper where it dissolves in hot (160° F.) mother liquor 3 from the end of the borax refining process. Repulped borax is then pumped to a hot dissolver, where steam injected directly into the tank raises the temperature to 200° F., and all borax goes into solution. Pachuca walls and agitation give proper mixing. The crude borax solution is polished in pressure filters and pumped to the CBL storage tank.

Next step is crystallizing refined borax. Temperature of the crystallizers determines whether pentahydrate or decahydrate comes down. Slurry from the crystallizers flows by gravity through a seal leg and into a centrifugal feed cone (10 feet high, 16 feet in diameter at the top) for thickening before centrifuging.

Final dewatering of refined borax takes place in seven centrifuges, five Sharples machines and two Cresson-Morris ones. In pentahydrate runs, slurry temperature must be high to prevent the pentahydrate from changing to decahydrate. A pentahydrate cake which is undergoing a phase transition to the decahydrate rapidly sets to a concretelike consistency, and the centrifuges would be badly damaged when unloaded.

Settling cone overflow and centrifuge filtrate and washings are combined as mother liquor 3 and pumped to storage. ML-3 goes from storage as required to the repulper to dissolve a fresh crop of crude pentahydrate. It is also the purity control stream in borax refining.

Centrifuges dump to conveyors on the floor directly beneath, and moist borax goes either to dryers or directly to the

boric acid and anhydrous borax plants.

Moist borax runs 5 to 6% free water from the Cresson-Morris machines, about 3.5% from the Sharples. Two double drum dryers and a tray dryer are used for drying the products.

The double rotary drum dryers are actually two drum dryers superimposed, with the discharge end of drum No. 1 immediately above the feed end of drum No. 2. This means moist borax enters the feed end of No. 1, flows down through it, and then drops into the feed chute to the high end of No. 2. Here, partially dried borax reverses direction 180° to flow down No. 2 drum. Hot air, meanwhile, feeds to both drums at their closest point—namely, the discharge end of No. 1 and the feed end of No. 2. Air thus flows countercurrent to borax in No. 1 and concurrent in No. 2.

Dry borax discharges from all dryers at about 120° F. Screw feeders move dry borax from the dryers to an elevator for conveying to upper levels for screening.

Prior to final screening, three magnetic separators operating in parallel remove iron.

All refined borax products are stored in bins with a combined capacity of roughly 26,600 tons. Products are shipped in bulk, bags, and drums, depending on customer preference.

Anhydrous Borax

Another boron plant section at Trona makes anhydrous borax or borax glass by driving off all water of hydration. The anhydrous borax process (Figure 2) starts at one of two calciners where about 70% of the water of hydration is removed from sodium tetraborate decahydrate. Feed to the anhydrous borax plant may be either coarse granular decahydrate from borax plant storage or wet, unscreened decahydrate from the borax plant centrifuges. Fine granular borax, powdered borax, and borax pentahydrate cannot be used as feed. They all puff excessively to make a very light calcine that blows out through the calciner dust collectors and into the wet scrubbers. Also, a light calcine cannot be used as furnace feed, because it will not seal the furnace feed ring.

Table II. Analysis of Borax Plant Liquors

Chemical	ML-1	ML-2
Borax [$\text{Na}_2\text{B}_4\text{O}_7$]	9.77	7.16
Potassium chloride	11.67	11.82
Sodium chloride	6.77	7.38
Sodium carbonate	6.57	7.55
Sodium sulfate	1.93	1.99
Sodium sulfide	1.00	1.01
Potassium bromide	0.96	0.99
Phosphorus (as P_2O_5)	0.46	0.49
Iodine	0.070	0.071

Calciners are 8 feet in diameter and 70 feet long. While there is no pronounced wet end as is often found in calciners and dryers, each calciner has two knockers to stop any build-ups. Hot exhaust gases from the fusion furnaces supply heat to the calciners, with the two larger furnaces "heating" one calciner each. Gas, at 1300° to 1500° F., is drawn into the calciners by direct induction fans. Flow is concurrent with the calcine.

Coarse granular borax from storage or moist borax from borax plant centrifuges is conveyed from the borax plant to the anhydrous borax plant across a weigh feeder to storage in two calciner storage bins, one for each calciner. A variable speed chain feeder moves borax from the calciner storage bin



Anhydrous borax is made in this large fusion furnace. Feed hoppers (top center, behind guard rail) continuously circle the furnace and distribute calcined borax into the furnace bed. Large diameter flue (lower left) supplies hot gases to calciners



Refined borax is dried prior to being conveyed to storage. In addition to dryer shown, American Potash also uses two double rotary drum dryers

to a calciner feed screw which charges the calciner.

Some puffing and dusting will inevitably occur during calcining, despite the best of feeds. Therefore, dust-laden exhaust gases from each calciner pass through a cyclone separator and then into wet scrubbers. Dust collected by the cyclone joins calciner discharge. Water in the wet scrubber recirculates and is continuously bled off and piped to the borax plant where it is used as process water. Scrubber water is made up with brackish well water.

Water remaining in the material leaving the calciners is then removed during fusion. Calcine is sent via a cross conveyor belt and an inclined conveyor to a distributing system of conveyors where it can be diverted to any one of the calcine storage bins for each of the three fusion furnaces.

Operating principle of each of the fusion furnaces is identical, though furnaces differ in construction detail.

Each has an inverted firebox surrounded by a cylindrical air box (Figure 2). Firing is by natural gas at the top of each.

The furnace bottom into which calcine feeds for fusion is bowl-shaped and water-jacketed. There is a gap of about 8 inches between the outer, bottom edge of the firebox and the top, inner edge of the furnace bottom. Directly above this gap is the furnace feed ring. Three feed hoppers continuously circle the furnace on the feed ring and distribute calcine into the furnace bed so that it completely fills the gap between firebox and bottom. As each traveling feed hopper passes beneath the furnace calcine storage bin, a cam opens the gates and calcine refills the traveling feed hopper.

At the bottom center of the borax bed is a water-jacketed lip ring. Molten borax flows down the calcine bed, over the lip ring, and into the furnace nozzle. Exhaust gases from the furnace exit in a

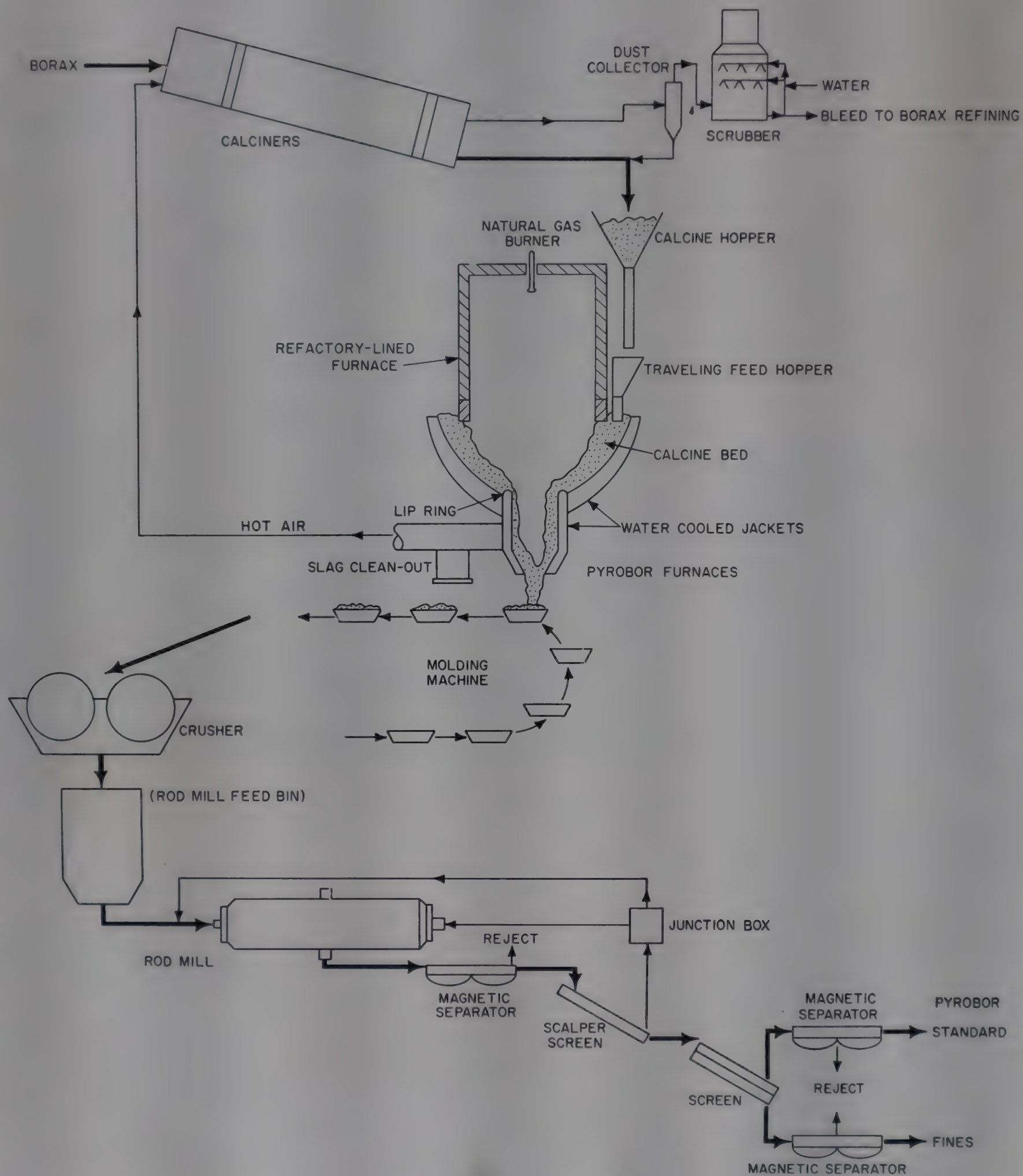


Figure 2. Flowsheet for production of anhydrous borax at Searles Lake, American Potash & Chemical Corp., Trona, Calif.



Anhydrous borax discharges from one of the furnaces into bucket conveyor. By the time buckets reach the discharge point, the borax has cooled to crystalline form, which is easier to grind



4-foot-diameter flue leading off the furnace nozzle. Flues on the furnaces carry hot gases to the two calciners.

Anhydrous borax may be made either as an amorphous glass or a crystalline solid. The glass is very hard to grind, and it abrades grinding equipment badly. The crystalline material, by contrast, grinds easily. To crystallize molten anhydrous borax, it may be stirred, seeded, or allowed to retain small amounts of water when molten. It must also cool slowly.

American Potash makes use of the last two conditions to operate furnaces No. 1 and 2 to make a crystalline product, while furnace No. 3 makes a glass. The design of the furnace bed is such that the borax flows off of the bed surface and out of the furnace as soon as it is liquid enough to do so, and sodium tetraborate at its melting temperature of about 1370° F. loses the last traces of hydration water slowly. Molten borax attacks all known refractories rapidly, even the zircons. With surface melting, borax actually lies on a bed of borax rather than against the furnace shell.

Furnace temperature may hit 2200° to 2600° F. at the top of the firebox, while down at the fusion zone temperature is about 1800° F., some 430° F. above fusion point of borax. As firing is usually constant, furnace operators are concerned mostly with seeing that the furnace has a good borax bed. If the bed gets too thick, unmelted borax runs out the nozzle. If it gets too thin,

steel water jackets will overheat and be damaged or blow steam. Too, furnaces operate at a slight pressure—0.5-inch water—and the calcine bed seals the gap between firebox and bottom. If the calcine bed gets too thin, the seal will “blow out.” By adjusting feed hopper speed, furnace tenders keep a proper bed in the furnace.

Molten borax discharges from furnaces No. 1 and 2 to molding machines

where slow cooling promotes crystal formation. Molding machines are actually continuous bucket conveyors whose buckets serve as molds for casting crystalline anhydrous borax into ingots. Buckets move at about 22 feet a minute, and by the time any given bucket reaches the end of the conveyor where ingots discharge, borax has cooled and crystallized (ingots actually contain about 5% amorphous glass that comes from sudden



Anhydrous borax from one of the furnaces discharges to chill rolls where it is cooled rapidly to the amorphous form. Although amorphous borax is more abrasive than crystalline, it can be ground without trouble when cooled into thin sheet, shown on the apron conveyor en route to the crusher



Borate ester is filtered in a specially-designed drybox as a step in developing new boron products

chilling as the first borax flows into individual molds).

Borax ingots discharge to a tooth crusher where size is reduced to about $\frac{1}{16}$ inches. Crushed material is conveyed to a crusher storage bin.

Furnace No. 3 operates exactly like No. 1 and 2. However, instead of molten borax discharging to molding machines, it discharges to two large, water-cooled rolls. Here it chills rapidly to the amorphous state as it is rolled into sheets about $\frac{1}{4}$ inch thick. Although the material is amorphous and therefore very abrasive, it is easier to

crush since it has been rolled into sheets. The material is then crushed, screened, and stored (Figure 2).

Boric Oxide

Boric oxide (B_2O_3) is growing rapidly in its use as a starting material for various organo-borons as well as inorganic borons such as elemental boron, boron trichloride, and boron carbide.

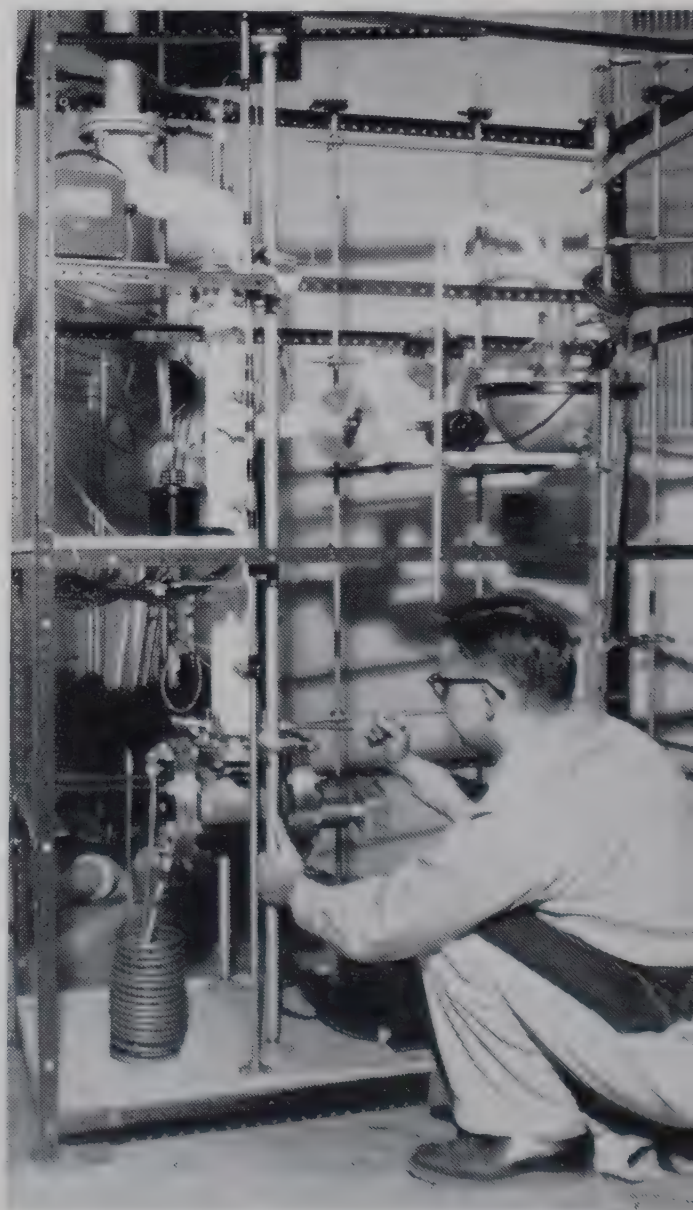
Boric oxide is produced by the dehydration of boric acid in a gas-fired furnace. The melt discharging from the furnace is passed over a chilling roll and is subsequently crushed and screened.

Materials of Construction

Most of the plant sections are made with standard materials—mild steel for tanks, pipes, and pumps; rubber for conveyors; wood for storage silos. Both the boric acid and anhydrous borax sections use special materials because of erosion, corrosion, or high temperatures.

In the anhydrous borax plant, furnaces No. 2 and 3 have fire-boxes of monolithic fire brick, and furnace No. 1 uses standard, super duty fire brick. Furnace shells are mild steel, and flues and thermocouple wells are Inconel and Type 446 stainless steel.

Abrasion causes lots of trouble in the anhydrous borax plant. Armor plate protects a number of chutes, and "cushion boxes" are placed at impact points on gravity handling equipment. Shape of these latter gives a recess at impact points. Recesses fill with product, and impact takes place on the product to reduce wear.



Last step in development of new product in American Potash's research laboratories is conducted with large scale equipment, so constructed to confirm information obtained on previous small scale research. If results are satisfactory, pilot plant is then constructed to duplicate actual production on restricted scale

What's in the Future?

As the world's second largest producer of borax, American Potash & Chemical Corp. is engaged in research to find new boron products and new methods to make existing boron products. This interest in boron products is a part of the company's long-range development and diversification program started shortly after World War II.

Since then, the company has spent an amount equal to about 3.5% of annual net sales for research. This compares with an over-all industry average of 1% for research and exceeds the chemical industry average of 3%.

The bulk of American Potash sales still rests with the company's "big five"—potash, soda ash, salt cake, borax, and lithium—but a steadily-increasing contribution to the company's annual income is being made by upgraded products, including new boron chemicals.

Boric oxide is being used in the manufacture of metallic borides. Small amounts of boron, usually in the form of ferro-boron because of cost, increase the strength of steel and reduce requirements for alloying elements such as nickel, chromium, and molybdenum. Another use is in making boron carbide,

one of the hardest man-made materials known.

Although some uses for elemental boron are classified under government restrictions, it is being used in fuses for rockets and flares and also as propellants for missiles and rockets. In atomic reactor shields, elemental boron combined with plastics provides effective protection from radiation and eliminates the need for weighty lead or concrete shields. It may play a vital role in a successful atomic reactor for aircraft.

The products described so far are in the inorganic field, and there are numerous others that the company is studying. Although the uses for these inorganic products are important, American Potash sees perhaps greater potential in organo-borons.

These organo-borons were experimented on from about 1840 to 1890, but little industrial application was found for them at the time. Renewed research indicates they will find extensive use in the petroleum, plastics, glass, and other industries.

The company's organo-borons fall into three general classes—borate esters, boroxines, and miscellaneous.

In the borate esters group are methyl borate and isopropyl borate, two of the

most important organo-boron products in American Potash & Chemical Corp.'s program. In addition there are butyl borate, cresyl borate, cyclohexyl borate, tetradecyl borate, plus some 20 lesser borate esters.

Information on many of the uses for borate is restricted. Outside the restricted classification, however, experiments are being conducted with methyl borate as a fungicide for citrus fruit. A small amount of the borate put in sealed shipping containers lowers spoilage by permeating the carton and combining with moisture from a bruise to seal off the bruise, thus preventing mold from forming.

Isopropyl borate, too, is important in the company's program. Nearly all borate esters eventually will probably be made from isopropyl borate because of higher yields and lower over-all cost.

Vital to the company's plans for isopropyl borate is that, as far as is known, no other producer has been able to manufacture this ester on a commercially practical basis.

The second organo-boron group is boroxines which include a number of compounds with a high boron content. Some organo-boron compounds have less than 1% boron, although generally they contain 3 to 4%. The boroxines, however, may have a boron content of more than 17%. With 17% boron, these boroxines are viscous liquids instead of solids, and comprise an entirely new group of boron compounds. The group is so new that few specific uses have been found as yet, but they will probably find widespread use in industrial processes where high boron content in liquid form is desired.

American Potash's third organo-boron group—miscellaneous—includes boron-phosphorus polymers, boranes, and boron-carbon compounds.

Although most of these compounds still are in the research or market development state, the effect of some are already being felt in the consumer market. One industrial application of boron chemicals was the development by Standard Oil of Ohio of the recently-introduced Boron Supreme gasoline, in which boron compounds provide added power for high compression automobile engines. This is one of the first commercial applications but it is not difficult to foresee the expanding effect throughout the petroleum industry.

Typical Analyses of American Potash's Boron Products in Per Cent

	Coarse Granular	Fine Granular	Powdered
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (equivalent)	101.2 ^a	102.2 ^a	103.89 ^a
NaCl	0.16	0.20	0.31
Na_2SO_4	0.03	0.05	0.09
Fe_2O_3	0.001	0.0007	0.001
	Standard V-Bor	Fine V-Bor, Refined Pentahydrate Borax	
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	101.8 ^a	101.9 ^a	
NaCl	0.08	0.11	
Na_2SO_4	0.019	0.039	
Fe	0.0007	0.0007	
	Pyrobor Dehydrated Borax		
	Standard	Fine	
$\text{Na}_2\text{B}_4\text{O}_7$	99.49	99.48	
Magnetic iron	0.00006	0.0004	
Acid insol.	0.0017	0.0010	
SO_3	0.05	0.053	
	Boric Acid		
	Granular Technical	U.S.P.	
H_3BO_3	100.0	100.0	
Na_2SO_4	0.08	...	
Standard U.S.P.—XIV and B.P. (1953) tests	...	Pass	

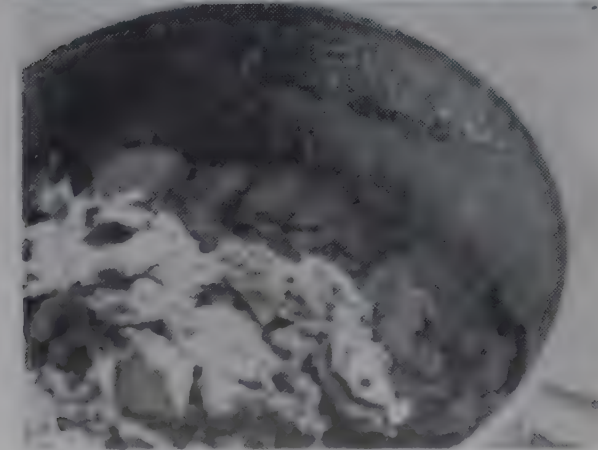
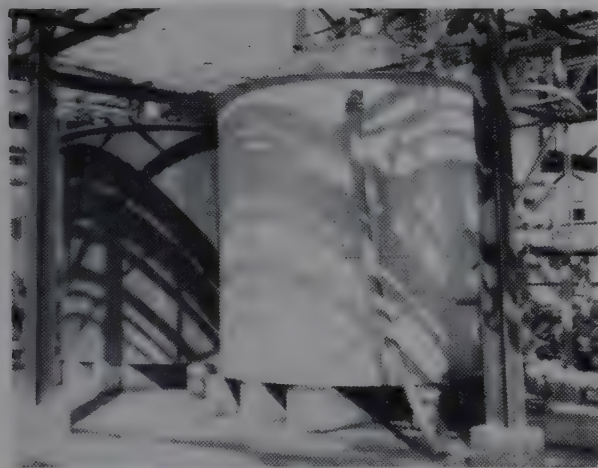
^a Dehydration during drying reflected in figures in excess of 100%.

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Uranium Recovery from Wet Process Phosphoric Acid



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In collaboration with

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PRODUCTION of uranium ore and concentrates in the United States rose rapidly during 1956 to the point where the U. S. now is the world's largest producer. Upon completion of new ore processing facilities and expansion of existing facilities, annual production in the free world should exceed 30,000 tons of uranium measured as uranium oxide (pitchblende) U_3O_8 , according to a speech, Atomic Energy and Mining, given by Commissioner Libby before the National Western Mining Conference at Denver, Colo., February 8, 1957.

Much of the U. S. present and near future uranium production will come from large ore deposits found over the past five years in the Colorado Plateau area (2). During 1956, U. S. uranium ore production reached an annual rate of almost 3,000,000 tons. It is expected to reach 5,000,000 to 6,000,000 tons annually, compared to 70,000 tons produced in 1948 (7).

Yet, in the interest of national security and to conserve a valuable raw material which would otherwise be lost forever, the U. S. Atomic Energy Commission has a long-range "insurance" program to develop other sources of uranium. One project aims at recovering uranium found in phosphate rock mined in Florida for manufacture of phosphate fertilizers and phosphate chemicals.

A By-Product of Phosphoric Acid

Manufacture. Uranium in phosphate rock could not be recovered economically today except that it is a by-product of phosphoric acid manufacture. Should the phosphate rock source be the only one available, however, then the rock might be processed for the uranium—with a significant increase in costs to any program for development of atomic energy.

Simple economic considerations will prove that recovery of uranium depends on manufacture of phosphoric acid. Less than two years ago, Jesse C. Johnson, Director of the Atomic Energy Commission's Division of Raw Materials, said uranium cost in a high grade concentrate may be considered moderate in 1980, if it is less than \$12 per pound at today's dollar value (7).

If low grade ore deposits were utilized, then a price of \$30 to \$50 per pound for uranium would remain reasonable. Higher "burn-up" or "breeding" may increase the fuel value for nuclear power reactors, permitting use of higher cost uranium without adding to power cost—thus a cost figure of \$50 per pound may be tolerated. Low grade uranium ores contain 2 to 10 pounds of uranium per ton of ore. A reasonable figure for phosphate rock is 0.2 to 0.4 pound of uranium per ton of rock. Therefore, uranium concentration in phosphate rock is one tenth to one fiftieth that found in Colorado Plateau ore.

To dissolve 1 ton of phosphate rock, roughly 0.8 ton of sulfuric acid is required. Assuming the acid satisfactory for rock acidulation costs \$20 per ton, then acid cost alone will be \$80 per pound of uranium recovered from phosphate rock should it be processed primarily as a source of uranium. Obviously any return on recovered uranium does not reduce manufacturing cost of phosphoric acid.

Five Plants to Date

To date, five companies have built plants designed to recover uranium found in phosphate rock. They include:

Blockson Chemical Co. (now owned by Olin Mathieson).

International Minerals & Chemical Corp.

Texas City Chemicals, Inc.

U. S. Phosphoric Products, Div. of the Tennessee Corp.

Virginia-Carolina Chemical Corp.

Blockson Chemical and International Minerals & Chemical recovery plants have been in operation for varying periods. The U. S. Phosphoric Products' plant is reported to have recently begun operations. Plants of Texas City Chemicals and Virginia-Carolina Chemical are reported not in operation pending revisions in manufacturing processes of major phosphate fertilizer and chemical products.

Uranium recovery operations vary among the plants of these companies. Slight differences in the phosphate rock as mined, differences in major products manufactured, and in process revisions by individual companies attribute to variations in recovery methods.

The Phosphate Rock

Prior to 1942, there was little interest in uranium. All the uranium needed to make radium for medical and scientific uses came from the Skinkolobwe Mine in Belgian Congo worked only part time. World War II made uranium a most important and strategic material, but no new sources were developed during the period from 1942 to 1948. The Manhattan Engineer District searched for uranium ores, but need for secrecy limited explorations to undercover operations. These investigations brought to light domestic phosphate and shale deposits that contained small quantities of uranium. Subsequent exploration throughout the world found the important deposits of higher grade ores in Canada, Belgian Congo, Union of South Africa, Australia, and Portugal, in addition to those in western United States.

At one time, it was thought that development of the low grade supplies would be necessary to meet uranium requirements for defense. With discovery

and development of more economic ores, this is no longer the case.

Even at early stages, large-scale uranium production from phosphate rock and shale deposits presented very difficult technical problems. It required large plant investment and use of much critical material. Still, preliminary studies were started.

First step was a survey of deposits containing uranium. The U. S. Geological Survey, cooperating with the AEC, found that the highest concentrations of uranium in phosphates occur in Florida's Pliocene Bone Valley formation, and the Permian phosphoria formation in Montana, Utah, Wyoming, Nevada, and Colorado. Tennessee phosphate deposits were found to contain very small amounts of uranium.

Western uraniferous phosphate deposits contain about the same amount of uranium as does Florida phosphate rock—0.1 to 0.4 pound per ton of rock. To date no significant quantities of uranium are recovered from western phosphate deposits.

Florida's phosphate deposits are of three general types—Bone Valley pebble phosphate, River pebble phosphate, and Hardrock phosphate. Of these, the Bone Valley formation lends itself best to large scale mining operations. It accounts for practically all of Florida phosphate production and about 80% of domestic production.

Geologists picture the formation of rock deposits as being stratified into four separate layers. Present day Florida phosphate mining operations involve the top 40 feet of the formation. Two top layers, considered overburden although they do contain some phosphate, are removed. The third layer—known as the matrix or apatite—extends from 24 to 40 feet below the surface and is the commercial bed of phosphate minerals.

The size of the materials handling problem may be seen from estimates of the amount of rock and waste removed. Annually the mining operations remove 46,500,000 tons of true overburden, 11,500,000 tons of leach zone material (containing some phosphate), and 30,900,000 tons of matrix. From the matrix, about 10,300,000 tons of 33% phosphorus pentoxide (P_2O_5) commercial rock concentrate are obtained. In this and in the leach zone material uranium content is between 0.2 and 0.4 pound per ton. Occasionally, a deposit is found with a uranium content up to 1 pound per ton.

U. S. Geological Survey estimates of recoverable phosphate reserves total about 5 billion tons containing 600,000 tons of uranium or an average of 0.25 pound of uranium per ton of phosphate rock. Of this amount, Florida matrix and Florida hardrock make up 2.4 billion tons. Because of this supply of uranium, the AEC developed processes to recover it from the Florida phosphate rock.

Process Development

Alkyl phosphates were long recognized as being able to extract uranium ions from solutions under special conditions. On this basis, the AEC contracted research to develop solvent extraction, along with other methods such as ion exchange, as a method to recover uranium from comparatively dilute solutions.

The Dow Chemical Co.'s Western Division research laboratory at Pittsburg, Calif., undertook an AEC contract in 1947 to develop methods for recovering uranium from low grade ores. Emphasis was placed on the phosphates. Their early research centered around precipitation and ion exchange processes. When it was noted that the ion exchange caused too great a dilution of the phosphoric acid, they changed to solvent extraction (5). The alkyl pyrophosphoric acids were found to extract uranium from phosphoric acid; therefore, this development was carried to the point where it could be piloted by the Florida phosphate producers such as IMC, USPP, and Armour. Later, additional work was carried out to show how the alkyl orthophosphates could be used to extract uranium from most any leach liquor.

Oak Ridge National Laboratory studied a number of organophosphorus compounds for extraction of uranium from phosphoric acid; but they never used the pyrophosphates.

Alkyl pyrophosphates with chains ranging from 4 to 17 carbon atoms have been investigated. The extracting power of alkyl pyrophosphates increases with increased chain length up to 17 carbon atoms. Physical properties of various alkyl pyrophosphates also affect the extracting power independent of the chain length. However, for economic reasons, octyl alcohol and isomers of decyl alcohol are mostly used.

Chemistry of Uranium Recovery

Florida phosphate rock as concentrated for phosphate fertilizer and chemical manufacture consists mainly of complex calcium phosphate-fluoride compounds with combined water of hydration. Substances found in minor quantities in the rock include organic matter, iron and aluminum oxides, calcium and magnesium carbonates, sodium, potassium, chromium, vanadium, uranium, and rare earth salts.

First step in winning the phosphates from the rock consists of digesting the rock with sulfuric acid under controlled temperature and concentration conditions to produce phosphoric acid and insoluble calcium sulfate (gypsum).

The initial acidulation releases about 70 to 90% of the uranium in the concentrated rock. Actual release depends on the oxidation-reduction conditions of the phosphoric acid manufacturing proc-

26% PHOSPHORIC ACID
CONTAINING URANIUM
AS U⁶ FROM
PHOSPHORIC ACID
PLANT

I/ICO

PLANT PROCESS SERIES

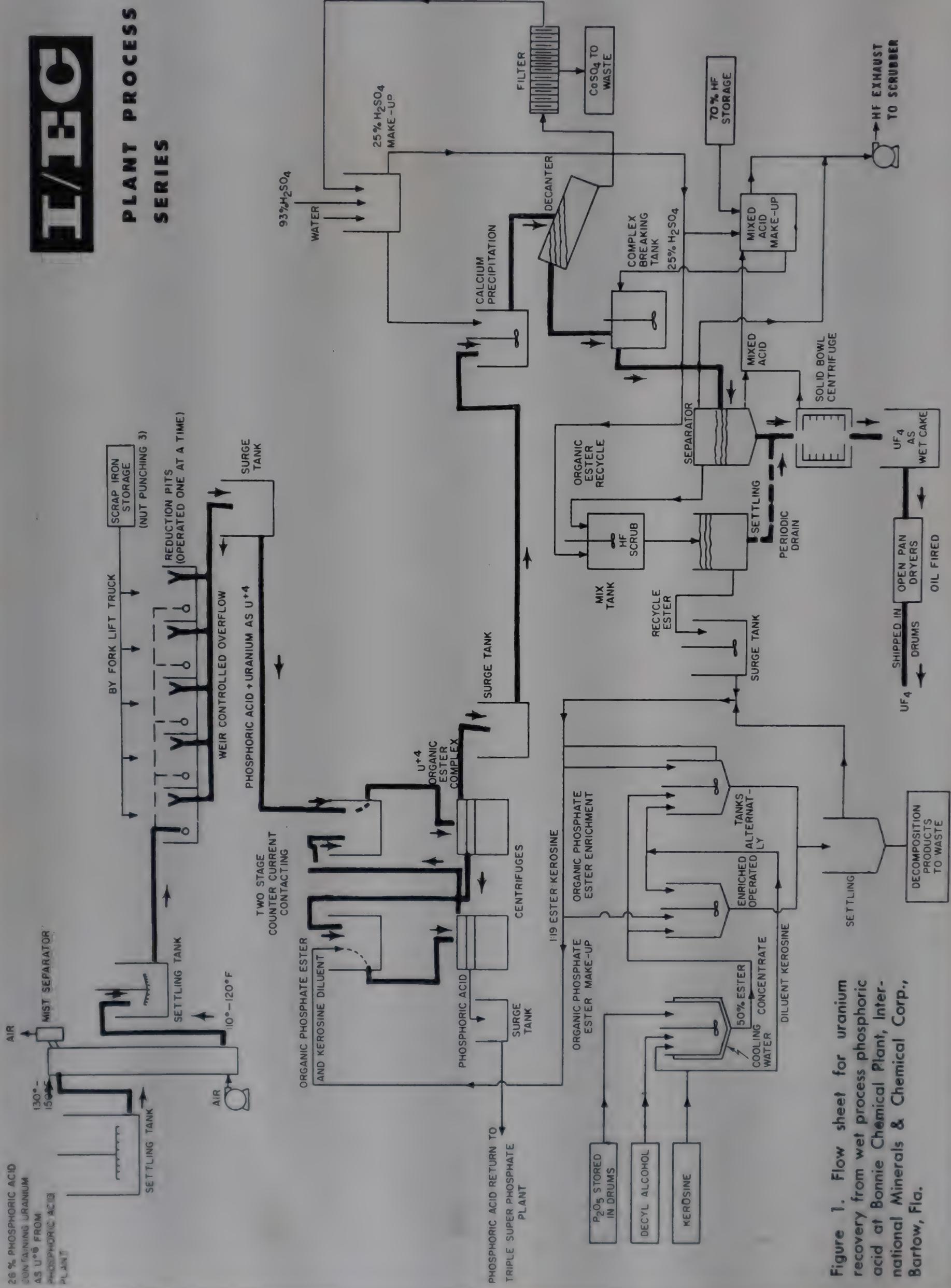


Figure 1. Flow sheet for uranium recovery from wet process phosphoric acid at Bonnie Chemical Plant, International Minerals & Chemical Corp., Bartow, Fla.

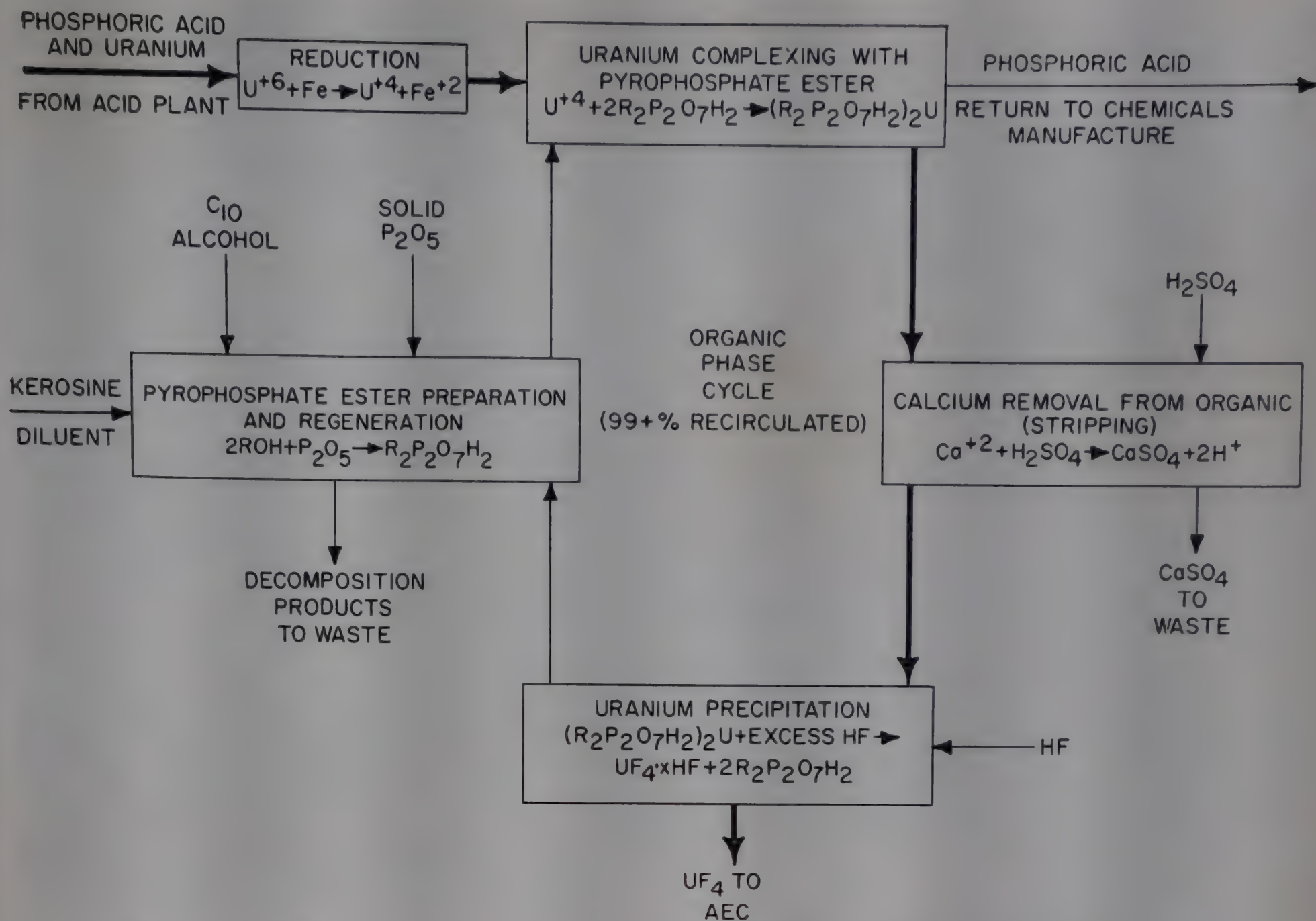


Figure 2. Important chemical processing steps in recovery of uranium from wet process phosphoric acid

ess. Computed as U_3O_8 , the resulting phosphoric acid solution contains from 90 to 200 mg. per liter.

To ensure that the maximum amount of uranium ion is in the tetravalent state, the solution is contacted with iron reducing the uranium(VI).

The phosphoric acid solution containing the reduced uranium ion is contacted with an alkyl pyrophosphate which has been prepared in an auxiliary step in the process. The alkyl pyrophosphate extracts the uranium from the phosphoric acid forming a complex compound with bonding similar to a chelate or a true chemical bond as in ion exchange. (The exact nature of the bonding in these complexes is not well understood.)

After separation from the phosphoric acid solution, the organic complex in a diluent has removed as much of other ions—calcium, iron, and others—as possible by precipitation with sulfuric acid. The uranium is then recovered from the complex by reacting it with hydrofluoric acid.

Some of the alkyl pyrophosphate hydrolyzes and is lost. The remainder is recycled for contacting more phosphoric acid.

Recovered uranium as uranium tetrafluoride, UF_4 , in a complex salt ($UF_4 \cdot xHF$) containing little free hydrofluoric acid, is dried and shipped to AEC installations for further processing.

Kerosine or a similar hydrocarbon fraction acts as a solvent for the alkyl pyrophosphate during contact with the phosphoric acid solution and for the resulting complex.

IMC's Process

International Minerals & Chemical recovers uranium as part of its phosphate chemicals manufacturing operations at the Bonnie Chemical plant near Bartow, Fla. (Figure 1).

Phosphate rock is digested with sulfuric acid under controlled temperature and concentration conditions, a process well-established for manufacture of phosphoric acid (3). The new phosphoric acid is filtered in a five-stage countercurrent repulping system (Figure 2).

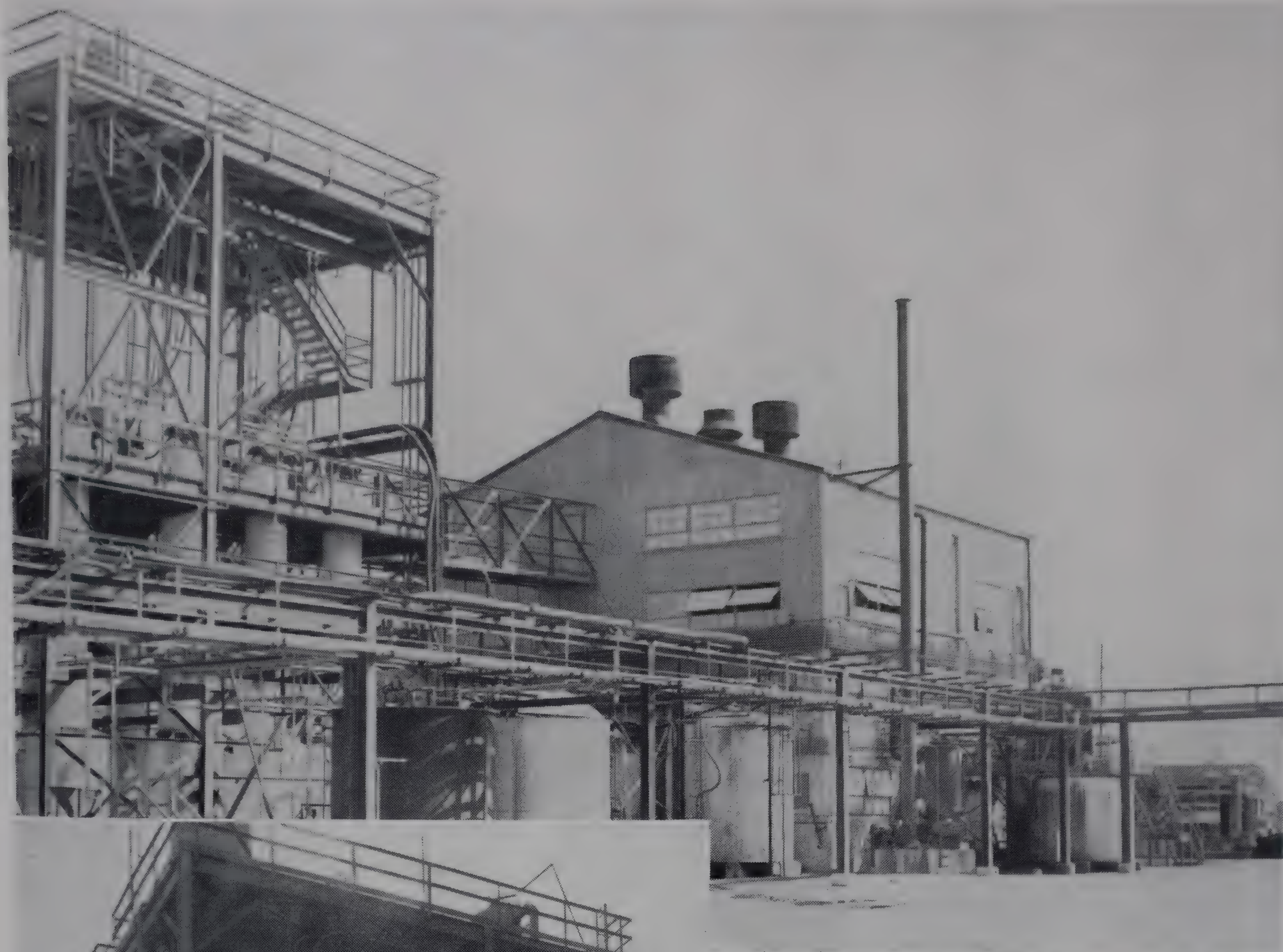
Filtered 26% phosphoric acid (as it is commonly called, although actual P_2O_5 concentration may vary from 24 to 28%) containing uranium(IV or VI) is pumped to a final settling tank, con-

sidered a part of the recovery plant. Uranium content averages about 0.0165% measured as U_3O_8 . Small quantities of other impurities also may be included in the phosphoric acid as it comes from the rock digestion plant.

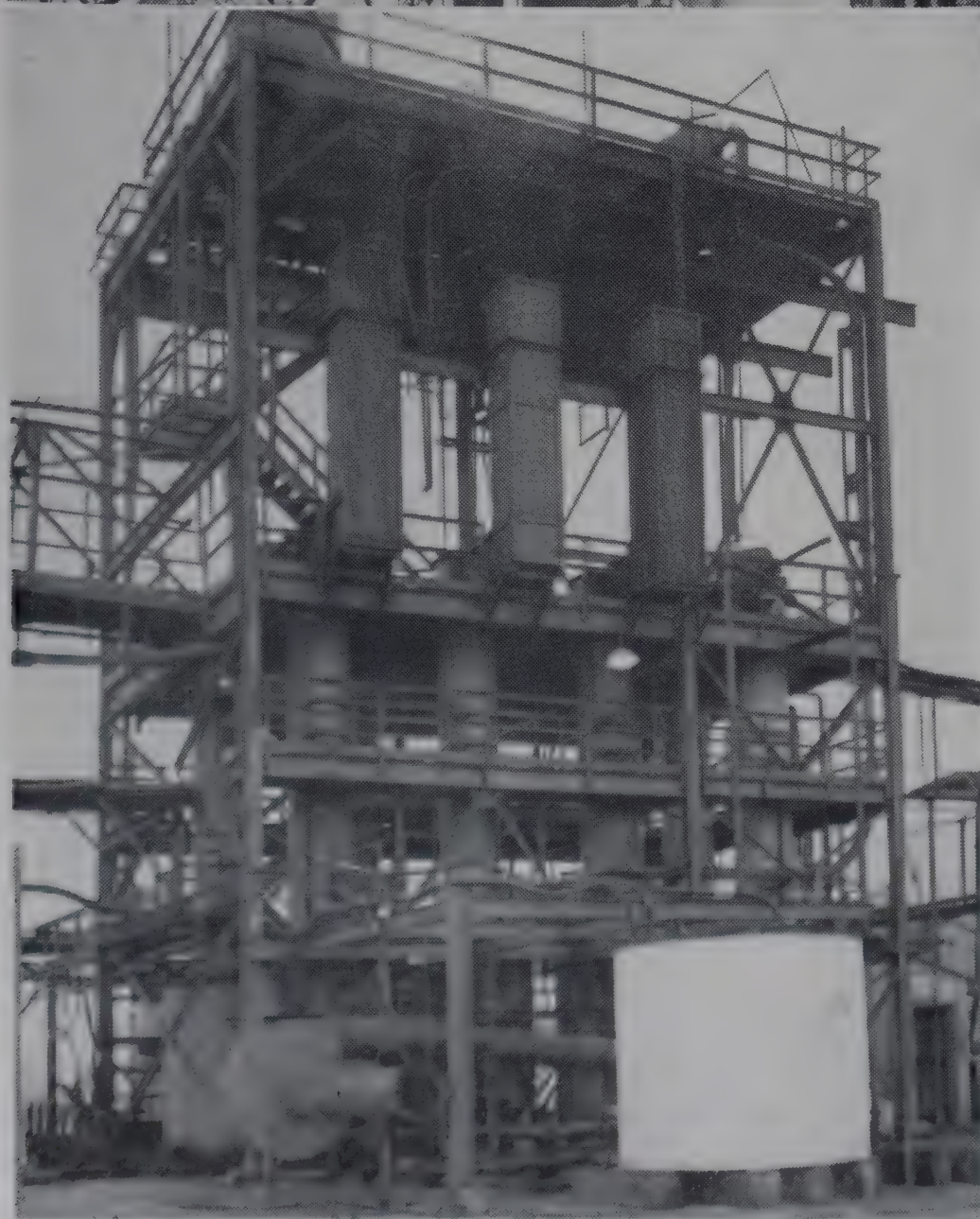
From the final 250,000-gallon settling tank in the phosphoric acid manufacturing plant, the incoming phosphoric acid goes to cooling towers in the uranium recovery plant. These towers, some of

Table I. Composition of Phosphoric Acid Solution to Uranium Recovery Plant

Component	Measured as	Per Cent by Weight
Phosphoric acid	P_2O_5	24 - 27.5
Fluorine	H_2SiF_6	1.5 - 2.2
Iron	Fe_2O_3	0.75 - 1.0
Sulfuric acid	H_2SO_4	0.2 - 1.5
Calcium	CaO	0.2 - 0.75
Aluminum	Al_2O_3	0.75 - 1.0
Magnesium	MgO	Less than 0.1
Potassium	K_2O	Less than 0.1
Sodium	Na_2O	Less than 0.1
Titanium	TiO_2	Less than 0.1
Thorium	ThO_2	Less than 0.1
Uranium	U_3O_8	0.0090-0.0200
Rare earths	Oxides	Less than 0.1



Uranium recovery facilities showing towers (left) used for countercurrent contacting step before installation of centrifuges, surge tanks, hydrogen fluoride exhaust blower and adsorption system, and solid bowl centrifuge (partially hidden by pipe rack)



Light colored tank stores phosphoric acid containing uranium before it goes to reducing pits or rotary reducer



Phosphoric acid containing uranium is cooled in the three towers (left) after coming from the phosphoric acid manufacturing plant. A single blower supplies air to each tower through a manifold. Rectangular boxlike items offset from each tower knock down entrained liquid from air stream



Scrap iron from nut punchings in bolt manufacture is put in these six reduction pits. Phosphoric acid containing uranium—some in hexavalent state—is contacted with the iron to reduce all uranium to tetravalent state before contact with pyrophosphate ester

which were originally used for the countercurrent contacting step, operate by allowing the acid to overflow a circular weir near the top into the rising air stream. Air cools the acid from 130° to 150° F. to 110° to 120° F. Cooling the incoming acid helps greatly to improve settling of the acid with subsequent reduction in the amount of scale found in lines and pumps.

From the cooling tower the acid goes to a 90,000-gallon settling tank with specially designed rakes to remove any settled solids. Flow through the tank averages 200,000 gallons per day.

Uranium in the phosphoric acid is not analyzed continuously as to how much of it is in the tetravalent or hexavalent states. For maximum efficiency in extraction, all uranium should be in the tetravalent state. To ensure the most possible quantity of uranium is in the tetravalent state, the acid goes from the last settling tank to a reducing step. Iron from punchings of bolt manufacture reduces the uranium. The reduction is done in "reduction pits."

The reduction pits are concrete and brick-lined, 5 feet wide and 8 feet long. Depth of iron punchings in a pit varies from 24 to 42 inches depending on how long the pit has been on stream. The phosphoric acid containing uranium is pumped in through a submerged distribution pipe. A weir controls outflow.



Decyl alcohol (mixture of trimethyl heptanol isomers) and 70% hydrofluoric acid are stored in these tanks



Actual extraction of uranium from phosphoric acid is done in two-stage countercurrent contacting process using pumps and centrifuges (left and right) which are on stream. Center centrifuge and one not shown replace these when cleaning and maintenance is necessary

Each pit is covered with a hood and two exhaust fans remove hydrogen generated during the reduction process.

One or two reduction pits are on stream at a time. Others are being cleaned and recharged with fresh iron punching brought by lift trucks from storage. One pit is always maintained in stand-by condition, cleaned and recharged, and ready to be put in operation. All pits are operated to have minimum iron

pickup consistent with maximum uranium reduction. Actually, pickup may bring iron content of the phosphoric acid to 0.1 to 0.3%. A pit remains on stream from 1 to 2 weeks depending on the operating efficiency of acid plant filters and uranium recovery plant thickeners.

From the reduction pits the phosphoric acid containing reduced uranium goes to a surge tank in preparation for the contacting step.

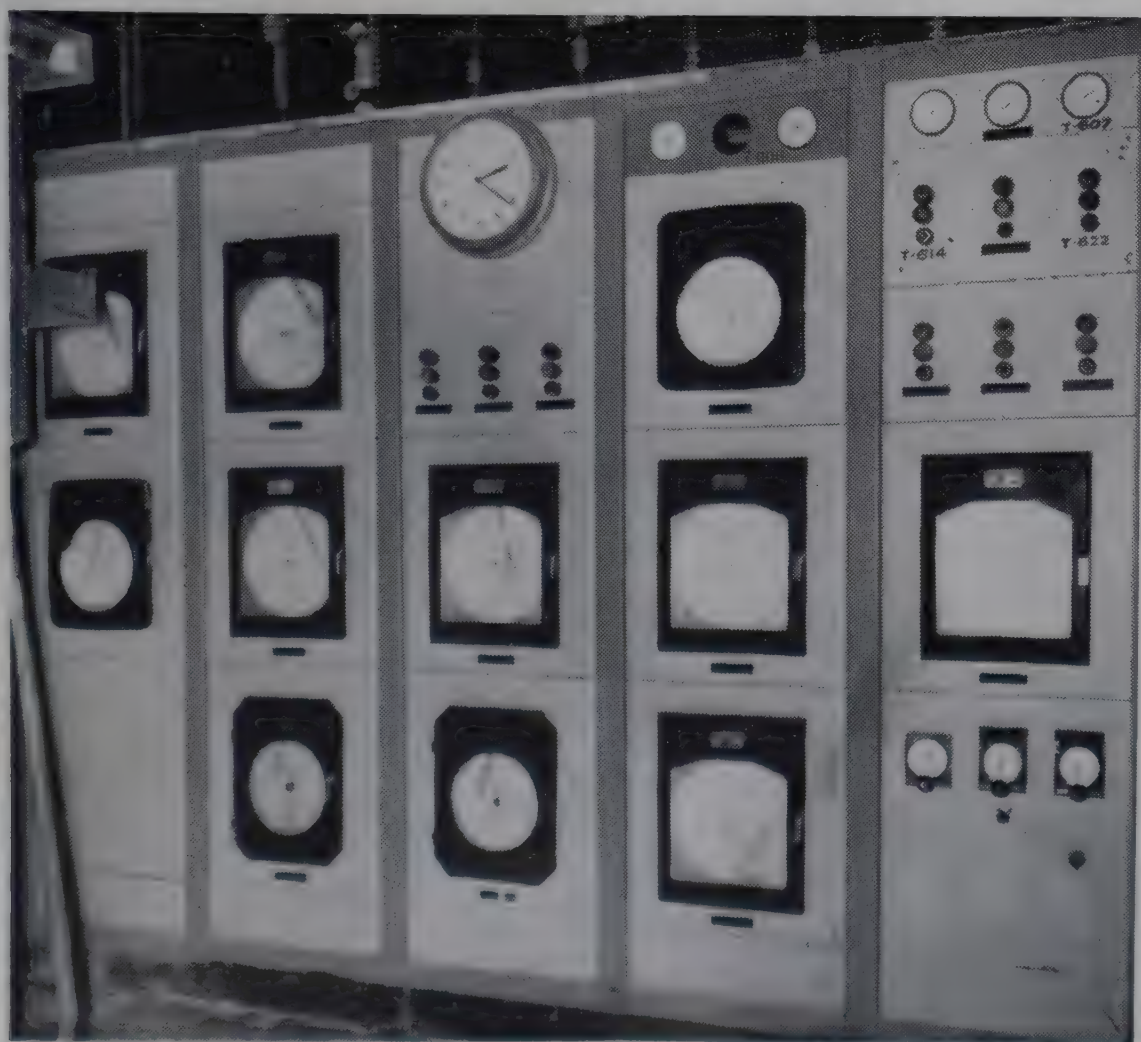
Contacting with Ester. Extraction of uranium from the phosphoric acid is done by pyrophosphate esters from a mixture of isomers of trimethyl heptanol, called "decyl alcohol." The extraction process is a two-stage countercurrent liquid-liquid extraction. The pyrophosphate ester phase (or organic phase) is about 10% of the total mixture. Pumping between surge tanks and phase separating centrifuges (3E) intimately contact the two phases.

The extracted phosphoric acid is returned to a hold-up tank and then goes to phosphate chemicals plant units manufacturing either triple superphosphate or dicalcium phosphate.

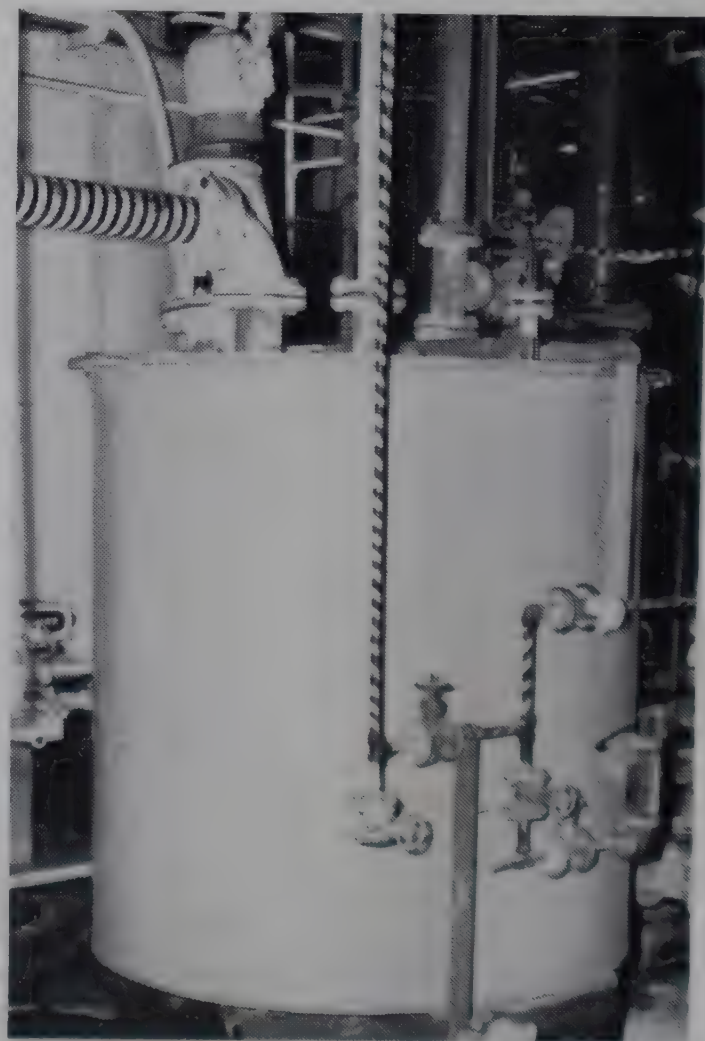
Calcium Strip. The pyrophosphate ester complexes small quantities of other metal ions in solution in the phosphoric acid.

Cooling after the final settling in the phosphoric acid plant and resettling removes a large part of the insolubles in the acid. However, maximum recovery of uranium and smooth operation of the recovery plant depend to an important degree on the minimum circulation of calcium and other ions through the process. A major difficulty decreasing over-all process efficiency occurs when too much calcium remains to be complexed by the pyrophosphate ester; this reduces the amount available to extract the uranium ion.

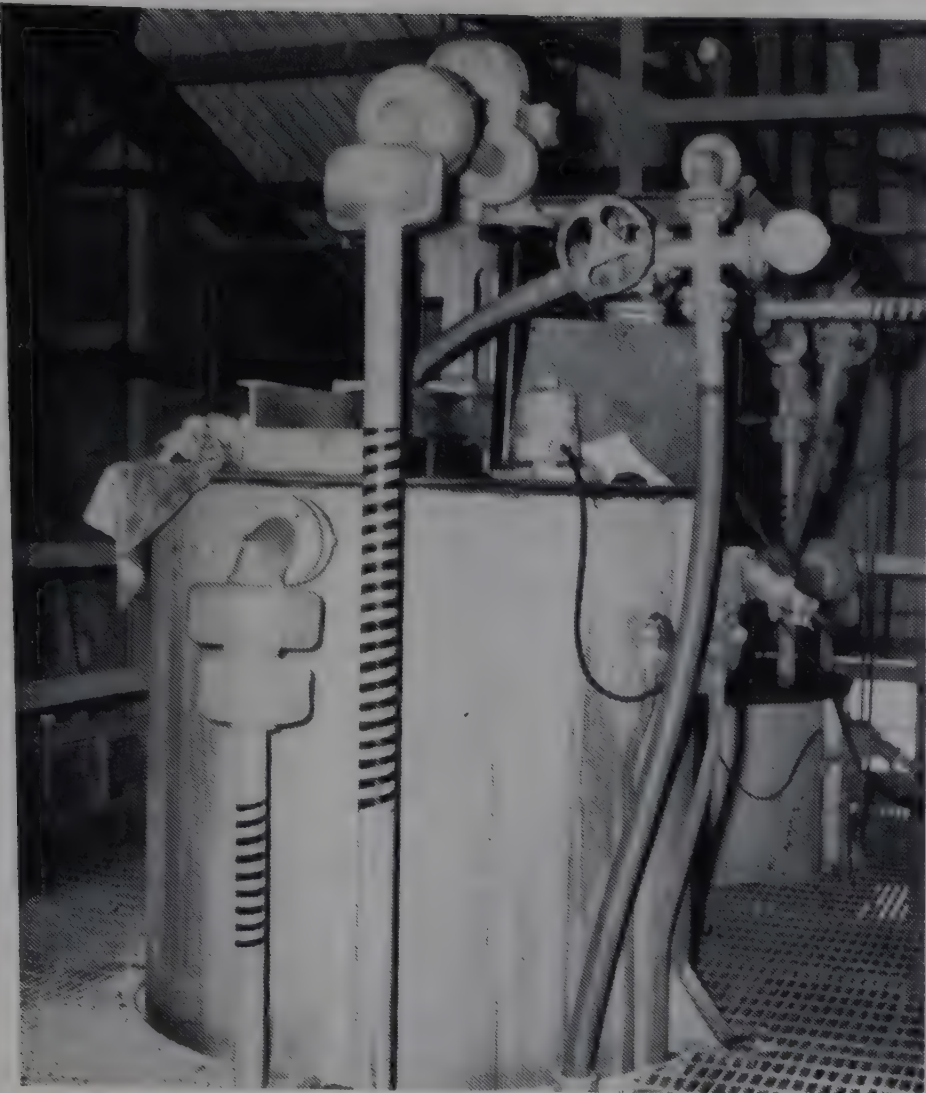
A second difficulty, occurring when more than a minimum amount of suspended solids gets into the organic phase,



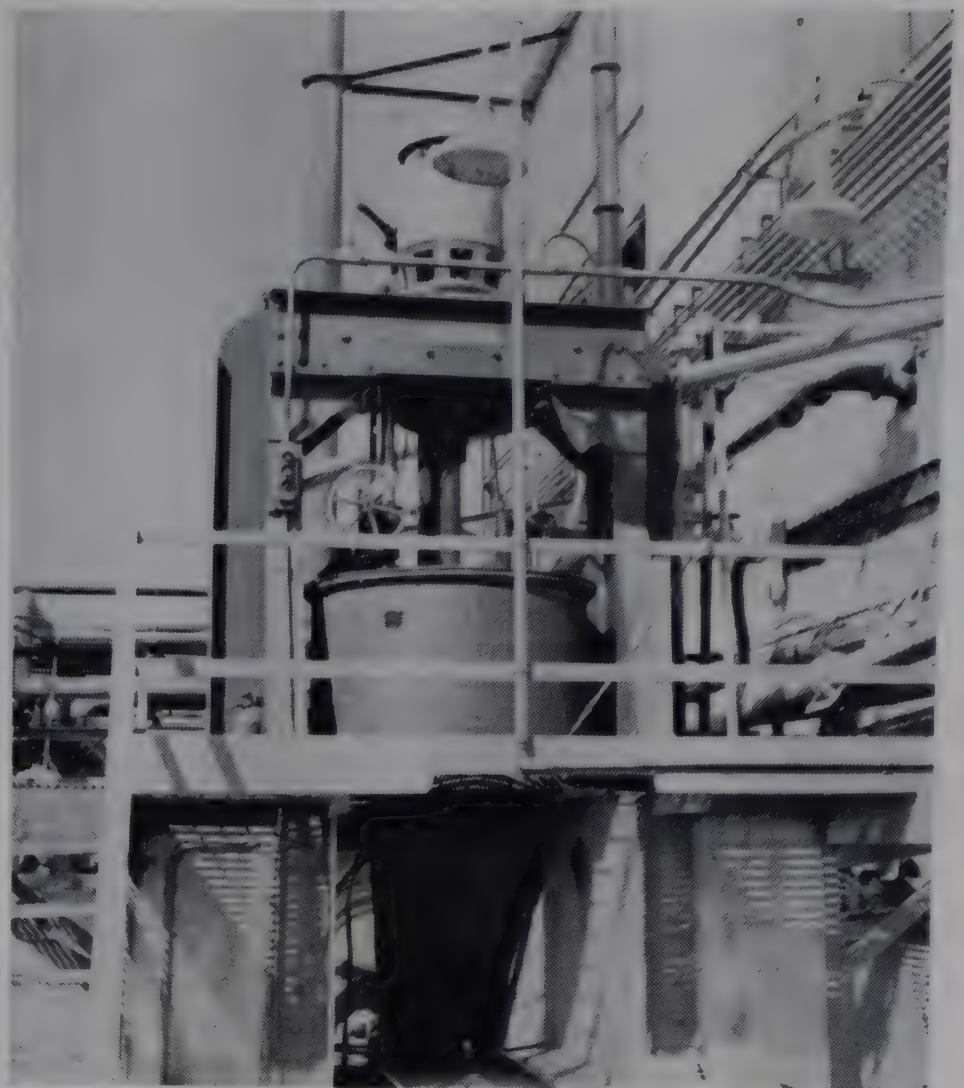
Control panel for recovery plant. Process control is achieved mostly through level and flow control, with wet chemical analysis used for quality control



Mixed acid (20 to 25% sulfuric and 15 to 20% hydrofluoric acids) are prepared in this tank. Lines with stripes carry hydrofluoric acid



In this tank, mixed acid is contacted with stripped organic phase to break the pyrophosphate ester complex with uranium. Lines with stripes carry mixed acid containing hydrofluoric acid or gas to exhaust



Solid bowl centrifuge separates uranium tetrafluoride from mixed acid used to precipitate uranium from pyrophosphate ester complex

is that emulsion problems become serious. Large quantities of emulsified organic phase in any tank or piece of equipment, which are level controlled, interfere with control instruments and operation of the recovery plant.

The pregnant organic complex passes to a mixing tank where an equal volume of 25% sulfuric acid is contacted with it to "strip" the calcium. Practically all calcium reacts to form insoluble calcium sulfate.

From the mixing tank, the pregnant organic complex and sulfuric acid solution go to a decanter. This saran-lined decanter, made especially for the calcium strip processing step, is a cylindrical tank inclined at about 30° with the horizontal.

Feed reaches the decanter somewhat above the mid-section. From the bottom of the decanter, the sulfuric acid solution containing the stripped calcium sulfate is pumped through a rubber-covered plate and frame filter press (4E).

The sulfuric acid solution from the filter press goes back to the 25% sulfuric acid make-up tank. The filter press requires dumping only once every 6 to 8 weeks—an indication of the small quantity of calcium that does pass through the thickeners. Actual dumping time depends directly, however, on the amount of calcium ion coming to the uranium recovery plant in the 26% phosphoric acid.

The level of the interface is controlled

in the decanter, as in other points in the recovery process, by the averaging specific gravity method.

Stripped pregnant organic complex comes off the top and goes to a complex breaking tank.

Breaking the Organic Complex.

Mixed acid, a solution of 20 to 25% sulfuric acid and 15 to 20% hydrofluoric acid, is used to break the complex and precipitates the uranium as the complex tetrafluoride with various molecules of hydrogen fluoride ($UF_4 \cdot xHF$). The

proportions of mixed acid and stripped pregnant organic complex are maintained so that there is an excess of hydrofluoric acid over that needed to bring out the uranium (15 to 30 times the stoichiometric quantity).

From the contacting tank, the mixture goes to a settling and decanting tank for separation. From the top of the tank, the organic layer is returned to make-up. From the side the mixed acid goes back to the mixed acid make-up tank. The precipitated uranium tetrafluoride settles



Uranium tetrafluoride is spread in trays for drying with direct-fired open pan dryers



After drying, uranium tetrafluoride is shipped to AEC in drums

to the bottom where it plus some mixed acid go to a solid bowl centrifuge (5E).

Final centrifuging is a batch operation. The centrifuge bowl contains a series of rings between which the uranium tetrafluoride cake builds up. As the space between each set of rings fills, separated mixed acid flows over the ring to the next space and eventually out the top. Effluent from the solid bowl centrifuge is returned to the mixed acid make-up tank.

When the centrifuge is full, it is stopped, and the cake is sampled and dug out. Wet uranium tetrafluoride cake (containing other salts also) is dried in outside open pan dryers. These dryers, fabricated in company shops, are heated by direct oil firing.

The centrifuging operation proceeds on a 12-hour cycle. Under normal conditions, the centrifuge bowl fills with uranium tetrafluoride in 10 to 12 hours. Then $1\frac{1}{2}$ to 1 hour is required to dig out the cake and prepare it for drying.

After drying, the uranium tetrafluoride is sent to an AEC installation for further processing. Because of its characteristic color, this product is the well-known "green salt."

Because of many variables in the processing operation, final product composition may vary widely. Calculated as uranium oxide (pitchblende), U_3O_8 , the uranium in the product sent to the AEC ranges between 45% and 55%. Fluorine content thus varies between 12 and 15% plus that of the combined hydrofluoric acid in the complex salts. Other compounds in the product include calcium (still as much as 5%), iron, aluminum, magnesium, sodium, potassium, thorium, yttrium in significant amounts, silica, and phosphates.

Organic Make-up. Preparation of the pyrophosphate decyl ester and compensating for loss due to hydrolysis constitutes the most important part of keeping the uranium recovery process efficient. The step of adding more phosphorus pentoxide to compensate for hydrolysis is known as "spiking" the organic phase.

As used for complexing uranium ion, the organic phase consists of 5 to 7% pyrophosphate decyl ester in a kerosine solvent. However, initial preparation takes place in 50% solution. This solution is diluted to 5% before addition to the phosphoric acid contacting tanks.

Initial make-up is done on a batch operation basis. Decyl alcohol and kerosine are mixed before adding phosphorus pentoxide. The reaction of decyl alcohol with phosphorus pentoxide produces an exothermic reaction. To maintain the mixture below 155° F., a water-cooled jacketed tank is used. Should the ester temperature rise and stay above 155° F. for any length of time, serious decomposition of the ester results. The formulation requires 2 moles of decyl alcohol to 1 mole of phos-

phorus pentoxide. Sufficient kerosine is used to equal the weight of pyrophosphate decyl ester formed.

Kerosine from storage and the 50 to 50 mixture of kerosine and ester go to the "organic spike" tanks at rates to maintain a 5 to 10% ester and 90 to 95% kerosine concentration in each tank. Each organic spike tank has a valve on the bottom through which aqueous acid phases picked up during the process and decomposition products formed during the spiking operation may be drawn off. Water and decomposition products plus a small amount of pyrophosphate ester drawn off from the spike tanks go to a settling tank. The ester is recycled to the return stream from main uranium extraction section of the plant.

The spike tanks act as storage for the pyrophosphate ester ahead of the tank where 26% phosphoric acid containing reduced uranium is contacted with the ester.

Removing HF from Organic Ester. After the stripped organic has been contacted with mixed hydrofluoric and sulfuric acids to bring out the uranium as the tetrafluoride, the mixture goes to a separator where the precipitated green salt and the mixed acid are removed from the organic phase. From the separator, the organic phase goes to a small tank where additional 25% sulfuric acid is mixed with it.

Small quantities of hydrofluoric acid and precipitated uranium tetrafluoride remain in the organic phase. Both materials must be removed to maintain high recovery efficiency. Should any hydrofluoric acid be carried over with the organic phase into the initial contacting stages, then some of the uranium will precipitate and separate in the centrifuge during the removal of the organic phase from the phosphoric acid. Should uranium tetrafluoride be carried from the last separator on around to the initial centrifuging, then it would also be lost.

After the organic phase is thoroughly contacted with more sulfuric acid, it goes to a settling tank. Periodically the acid and any additional precipitated uranium tetrafluoride is drawn from the settling tank and returned to the solid bowl centrifuge. The organic phase goes to a surge tank prior to being returned to the organic spike section.

Corrosion

Handling all the acids in this process requires use of the most corrosion-resistant equipment that is possible to obtain commensurate with capital investment. Tanks of all types used to handle phosphoric acid and the organic ester phase are made of mild steel and lined with saran. The filter press to remove calcium sulfate in the calcium strip section is rubber-covered steel.

Mild steel, saran-lined tanks are used

for mixing or diluting acids. Sulfuric acid comes directly from the acid manufacturing unit in the rock digesting plant, requiring no storage. The 70% hydrofluoric acid is stored in mild steel tanks under a dry atmosphere. Piping carrying 70% hydrofluoric acid is saran-lined.

Pumps handling process materials are of stainless steel or Karbate. Erosion coupled with or derived from corrosion presents only minor problems since fluids pumped in processing contain relatively small amounts of solids.

Doubling of tanks and stand-by equipment permits emptying tanks and shutting down equipment to allow repairs to be made on most units. During periodic shutdowns, all linings are inspected for damage and pumps, centrifuges, and filters checked for effects of corrosion.

Analytical Techniques

Various streams in the recovery process are analyzed on a routine basis. In addition to providing information to control process variables, periodic analysis of the main stream gives a measure of recovery efficiency.

The analysis work done in the recovery plant laboratory may be divided into three separate parts:

1. Feed and feed preparation analysis.
2. Process control analysis.
3. Auxiliary or service stream analysis.

Most important, obviously, is analysis of the 26% phosphoric acid stream to the recovery plant for its uranium content. This is done by a fluorimetric method. The instrument used for determining feed stream uranium content is a modified U. S. Geological Survey Model VI transmission fluorimeter (4).

The only other material in the feed determined is ferric oxide which is analyzed for by usual titrimetric methods.

The reduction of uranium with iron step is considered as a feed preparation process in that it occurs before the 26% phosphoric acid and decyl ester phases are contacted. Therefore, the "reduced acid" is analyzed at this point for iron(II and III). This gives a check on the pickup of iron from the reducing pits and an indication of how much may be found in the pregnant organic stream later. High or low iron in the reduced acid also shows improper operation of a reducing pit (most likely) and thus indicates that a pit should be taken off stream for cleaning or that the distribution system for 26% phosphoric acid in the pit may be operating incorrectly.

Process Control Analysis. First analysis made on the process stream is the raffinate from the last centrifuge. Determination of uranium in the phosphoric acid returning to the phosphate chemicals plant with the fluorimeter gives a measure of the theoretical uranium recovery from the 26% phosphoric acid.

As a check toward a material balance

on the uranium recovery from the phosphoric acid, the pregnant organic stream is also analyzed for uranium fluorimetrically. Samples are taken from the surge tank after the extraction step. Analysis of the organic before spiking for uranium completes the material balance.

Before shipping, the dried green salt is checked for actual uranium content. The method used for this analysis is the standard cupferron procedure modified by Rodden (6).

Auxiliary Stream Analysis. By analyzing materials used to service the pregnant organic stream, both auxiliary stream control and an ideal process efficiency are obtained. The strip sulfuric acid is checked for strength. Mixed hydrofluoric and sulfuric acid get routine checks on concentrations to ensure that the precipitation proceeds satisfactorily. Should hydrofluoric acid concentration drop too low, incomplete precipitation would result, with loss of uranium recovery efficiency. If the hydrofluoric acid concentration goes too high, then hydrolysis of the alkyl pyrophosphate ester becomes serious. Another material analyzed for in mixed acid is iron.

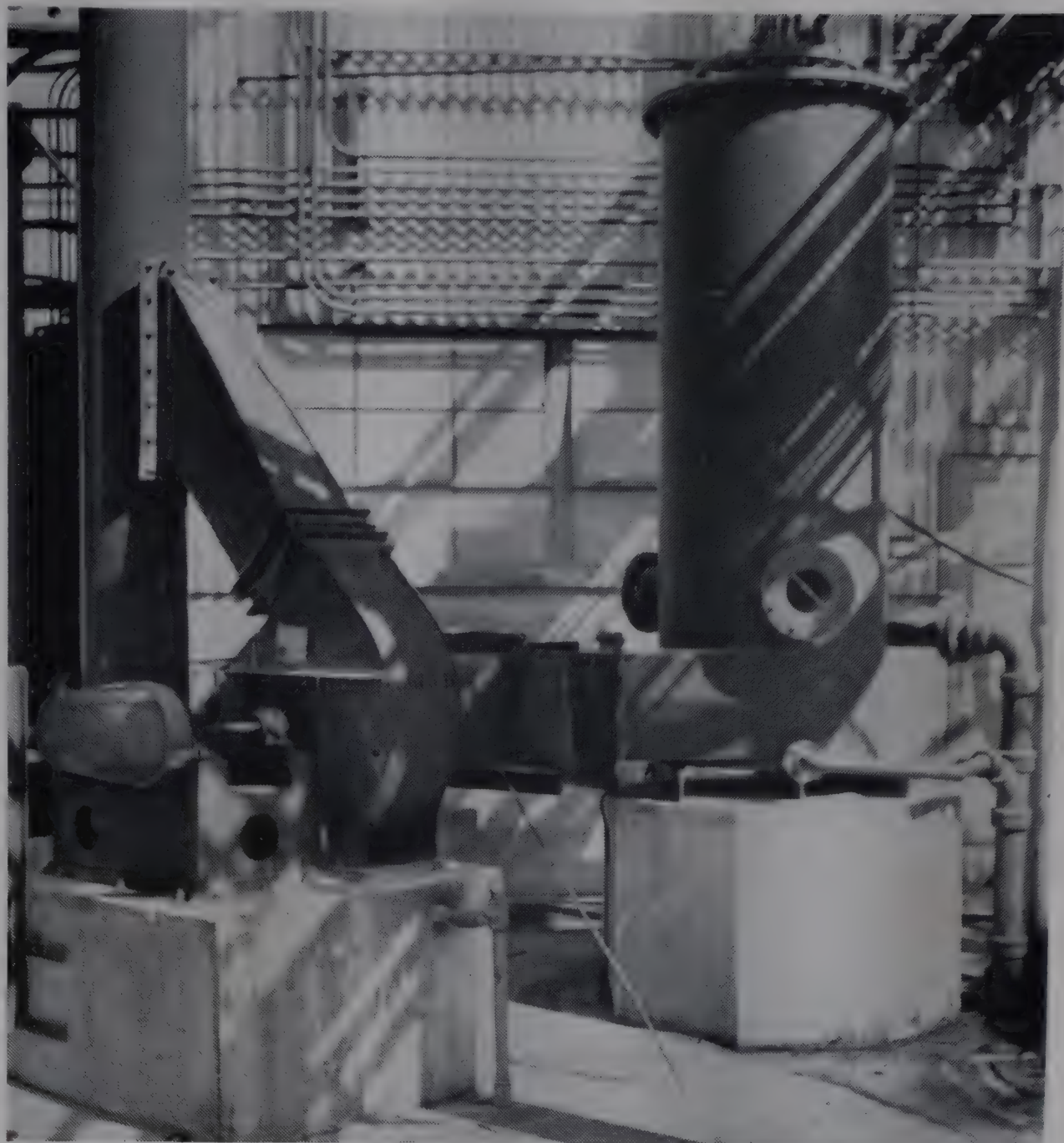
Routine checks are made on the scrub acid used to remove any hydrofluoric acid carried over in the organic phase after uranium tetrafluoride has been separated. Effluent from the scrub tank is checked for fluorine content. Sulfuric acid used for scrub has its concentration determined routinely. Build-up of uranium likewise is checked to determine when the scrub tank needs to be cleaned to prevent loss of uranium with the returning organic phase. Scrub acid is occasionally checked for iron and aluminum.

Samples of organic stream from the surge tank before going to spiking are analyzed for phosphorus pentoxide to determine the amount of spike needed. Here also checks are made for iron and aluminum oxides. On a routine basis, most analyses are made by fluorimetric methods or by wet chemical methods.

For convenience in determining efficiencies of various operating units and process steps, analyses are recorded on graphs. Survey of analytical data aids in making decisions to take a particular unit off stream for cleaning or repair. Correlation of data has also permitted a reduction in the frequency of some analyses from that used when the recovery plant first went into operation.

Handling Hydrofluoric Acid Fumes

Major source of possible irritation to operating personnel comes from hydrofluoric acid gases which escape from the mixed acid used to precipitate the uranium from the pregnant organic complex.



Fumes from tanks are passed through absorber (right) to remove any HF, which may be released. Left, blower and part of stack

All tanks and equipment handling hydrofluoric acid or materials which may release it are covered and connected to a fume scrubbing system. These include the mixed acid contacting tank, the separator for uranium tetrafluoride, organic ester, and mixed acid, and the mixed acid make-up tank. In addition the Tolhurst centrifuge is connected to the scrubbing system.

The hydrofluoric acid is absorbed in water, neutralized with lime, and sent to a sewer returning to treatment facilities in main phosphate chemicals plant.

Absorption of hydrofluoric acid and cooling of the make-up tank for the decyl ester constitute most of the use of water—100 to 200 gallons per minute—in the uranium recovery plant.

Recovery Plant Start-up

The uranium recovery plant is designed to operate continuously. However, since it is dependent on the phosphoric acid plant for 26% phosphoric acid as the basic raw material, and in spite of doubling or substituting equipment, complete shutdowns of the plant do occur.

First step in starting up the recovery

plant consists of preparing the service streams—organic ester, 25% sulfuric acid, and mixed acid. Preparation of the organic ester begins batchwise in the tank where the solution strength can be kept at 50%. As batches are made, they are pumped to the spike tanks and diluted in preparation for contacting with the phosphoric acid. Start-up requires a minimum of 6500 gallons of organic ester. During operation the only additional organic ester needed is to replace entrainment and degradation losses. These losses total less than 0.5 to 1.0% by volume of phosphoric acid processed.

Acids preparation merely requires dilution of acids from the sulfuric acid plant manufacturing unit or stored 70% hydrofluoric acid.

While the service streams are being prepared, 26% P_2O_5 phosphoric acid is brought from the phosphoric acid plant, cooled, and settled. Then the 26% phosphoric acid goes to one or two of the reducing pits to bring the uranium to the tetravalent state. The number of pits put on stream initially depends on the phosphoric acid flow, acid temperature, and the condition of the pit or pits.

From the reduction pits the phosphoric

acid goes to the contacting step. Then the entire process goes on stream as tanks, lines, and other equipment fill-up. The total time required to bring uranium tetrafluoride to the final centrifuge is approximately 24 hours. However, about 3 days of operation is needed to establish equilibrium at a high efficiency level.

Maintenance

Although the most corrosion-resistant equipment available is used, corrosion and its prevention present the major maintenance problems. Routine inspections and analysis during operation prove to be a valuable aid in detecting corrosion. During shutdowns, maintenance crews inspect all equipment for corrosion and repair or replace worn parts.

Equipment that is doubled or that can be taken off stream long enough gets periodic inspection and cleaning. Equipment, such as pumps, and agitator drives that can be lubricated while operating, receive routine attention.

Scale. Next to corrosion, scale presents serious operating and maintenance problems. Scale results from the many compounds of limited solubility carried through the process.

Control valves scale up and become limited in their operating range or completely inoperative. To clean the valves, they must be removed from the line and the scale scraped out. Scale in lines requires periodic boiling out with water or chipping to open lines.

As operating skill of plant personnel developed, scale became much less of a problem than during the early initial start-up period. Temperature and flow conditions are now held more steady reducing precipitation of salts of difficult solubility. The cooling of the phosphoric acid step early in the process has contributed significantly to reducing the scale problem by improving the settling of insolubles in the final 90,000-gallon thickener.

Instrumentation

Compared to a refinery, instrumentation for the uranium recovery plant is simple. The most important control function is to control liquid levels in tanks and process equipment. Of lesser importance are temperature control of cooled tanks and feed to extraction centrifuges.

Tank level control is the basis for process rate and flow control. Flow raters give supplementary flow control and flow rate indication and record (1E).

Actual tank level sensing is done with dip tubes measuring differences in head pressures with pressure transmitters (2E). Generally this type of control has proved satisfactory.

Emulsion Problems of Interface Level Control. However, in controlling

tank levels where an interface exists, some difficulty arises occasionally. The tanks or equipment where an interface exists include the decanter in the calcium strip section, the settler for separating the precipitated uranium tetrafluoride from the organic phase, and the hydrofluoric acid scrub tank.

All these places where an interface level must be controlled have emulsion problems. Gravity differences of the organic complex and acid phases are sufficiently large (range is from 0.8 to 1.2) to present no detection problems. But difficulty arises when the quantity of emulsion in a tank becomes so large that the extent of the emulsion reaches to the ends of the dip tubes.

The emulsion problem becomes most serious in the separator following the complex breaking tank. Here, level control must be precise to separate essentially three phases. Difficulty arises when the finely divided uranium tetrafluoride increases the emulsion range. Slow settling of the crystals also contributes to the separation problem or removing the mixed acids so that a minimum amount of liquor must pass through the solid bowl centrifuge.

Research to date indicates that in the precipitation of uranium from the organic complex, several crystal forms of $UF_4 \cdot xHF$ exist. Some of these crystal forms come out fast and others more slowly, thus causing an emulsion problem.

Efforts to find a method to overcome the emulsion problem include investigations of chemical and mechanical techniques. No chemical emulsion breaker has been found completely and continually effective.

Future

Of several processes used today for winning uranium salts from naturally occurring deposits, solvent extraction is gaining in popularity (2).

Solvent extraction has several important advantages over precipitation or ion exchange methods for uranium recovery. These advantages include:

- Continuity of operation.
- Lower raw materials cost because of greater reagent recycling possibilities.
- Larger concentration effect than any other process.
- Extractant is less expensive than ion exchange resin.
- Little or no dilution takes place.

Admittedly, solvent extraction has drawbacks such as solvent loss is easier, danger of fire (kerosene), and a few ions poison the organic extractant (titanium and thorium). However, the first two of these possible drawbacks can be overcome by careful operation. Only small quantities of extractant poisoning ions are found in Florida phosphate rock making this difficulty minor.

IMC's uranium recovery plant at Bonnie has provided much opportunity to gain operating experience with the solvent extraction process, to discover weak points in the process, and to correct these by substituting improved equipment and/or operating techniques.

Dependent as it is on the operation of the phosphoric acid plant, the uranium recovery plant has performed well to date. Its capacity depends on phosphoric acid production, but the recovery plant handles 90% of the acid produced.

Actual recovery of uranium in the phosphoric acid feed to the plant varies widely. In early planning and experimental work, it was thought that about 50% of the uranium in the feed could be recovered. Now, after 18 months of operation, the plant can be expected to have a realistic maximum recovery approaching 75% of the uranium in the feed.

Based on this experience, other liquid-liquid extraction plants built to recover uranium from various sources have begun shake down operations. Construction of other extraction plants is under way but not necessarily based on IMC plant.

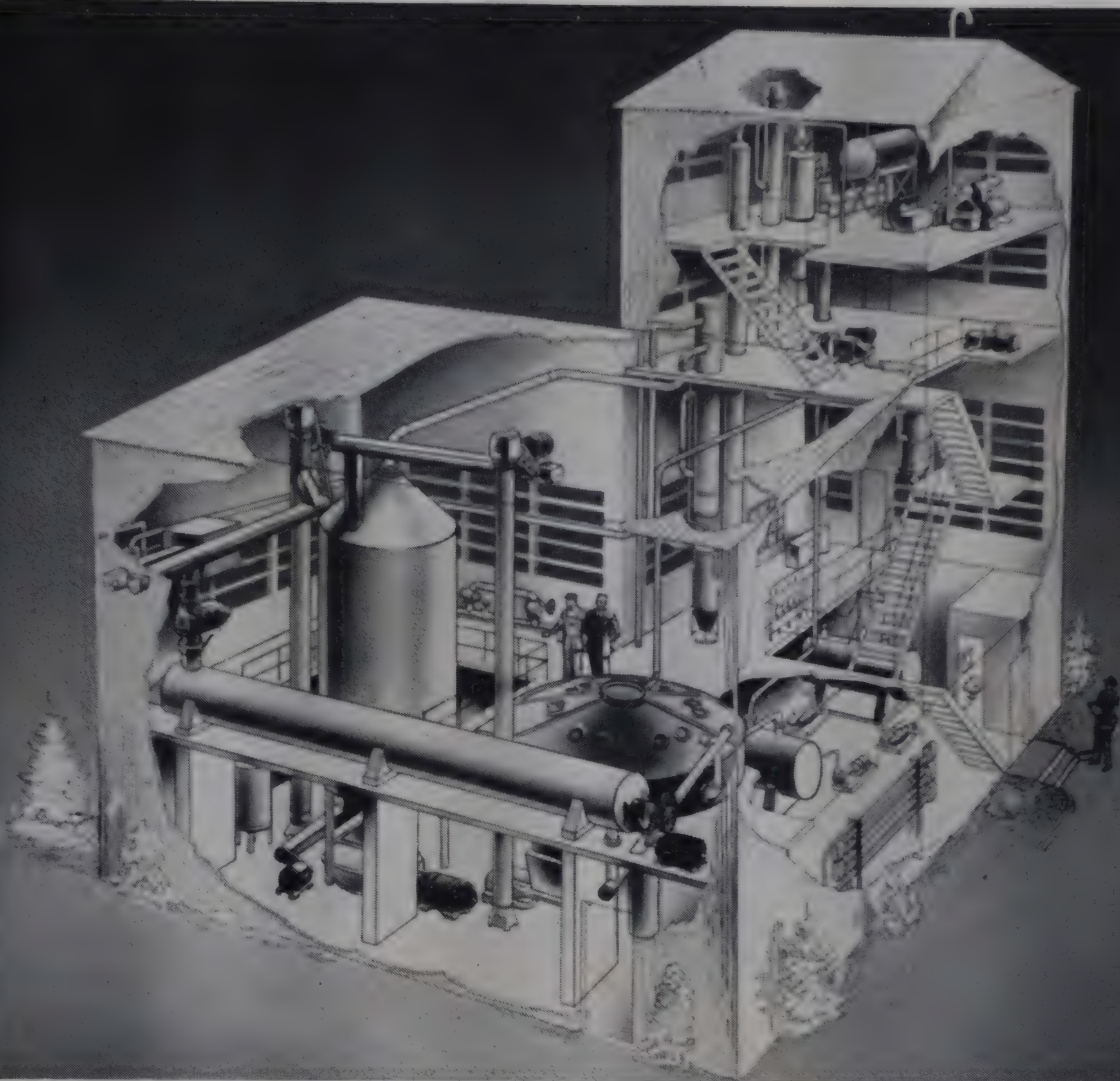
In addition to saving a valuable resource and partly satisfying a need for raw materials for nuclear energy production, the IMC uranium recovery plant contributes significantly to specialized process technology for recovery of products in small concentration contained with large quantities of other materials.

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Processing Equipment

- (1E) Fischer & Porter Co., Hatboro, Pa., flow meters.
- (2E) Moore Products Co., H and Lycoming Streets, Philadelphia 24, Pa., pressure transmitters for level indication.
- (3E) Sharples Corp., The, Philadelphia 40, Pa., Nozjector centrifuge, Model DH 2 S 6.
- (4E) Sperry, D. R., & Co., Batavia, Ill., plate and frame filter press.
- (5E) Tolhurst Centrifugals, Division of American Machine and Metals, Inc., East Moline, Ill., solid bowl centrifuge, 800 r.p.m., 15 hp.



Filtration-Extraction of Cottonseed Oil

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WHEN Eli Whitney invented the cotton gin in 1794 he opened up vast opportunities for cotton—the versatile fiber reigned as monarch of southern agriculture for longer than a century. His invention made available nearly two pounds of cottonseed for every pound of cotton produced. This oilseed has fired the imagination of scientists, taxed the ingenuity of equipment manufacturers, and challenged the resourcefulness of oil-mill owners and superintendents who wanted to use it for man's benefit.

Cottonseed processing, during its infancy, reflected the struggles of many

groups to establish oil mills in numerous southern locations (8). The first mill of any commercial importance was built at Natchez, Miss., in 1834. Yet in 1860, 66 years after invention of the cotton gin, this country had only seven active mills. After 1880, the industry developed at an accelerated rate; the maximum number of active mills, 885, was reported in 1914. The tonnage crushed reached its peak, 6,326,000 tons, in 1937, but by this time the number of operating mills had decreased to 466. Today the number of active mills is still declining; it is now about 300.

This decrease in the number of mills is a parallel development of a number of other changes. It does not signify a decrease in importance of the industry;

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it reflects many of the forward steps that have occurred or that are in progress. Improvement of rural roads is probably the most significant development that has enabled cottonseed oil mills to enlarge the area they serve.

Direct application of pressure, typified by hydraulic pressing, was the only method used to separate oil from the meal for many decades during the industry's early growth. Hydraulic pressing required a great deal of labor, but many hands were available. Almost until World War I, it seemed that hydraulic pressing would always be used for cottonseed processing.

Then mill owners began to consider screw pressing, which ever since has replaced hydraulic pressing to the extent that it is now the most popular processing method. Screw presses probably handled between 20 and 30% of the 1950-51 crop. Today about 35 to 45% of the crop is processed in screw presses.

Solvent Extraction for Cottonseed

As early as World War I attempts were made in the United States to apply solvent extraction to cottonseed. The first modern continuous installation was completed by Delta Products Co. at Wilson, Ark., in 1947. Five plants were in operation by 1950, and at that time

two of these plants used prepressing with screw presses. About 7 or 8% of the 1950-51 crop was processed by solvent methods.

Now a great change is in the making. Thirteen solvent-extraction plants operated during 1951-52 and only six of them used direct extraction. (The others employ screw presses for prepressing.) Today some 28 mills use solvent extraction; of these, 11 have direct processes. Their installed capacity of about 7000 tons per day represents approximately 40% of the crop being processed.

Cottonseed oil is normally worth about four to seven times the price of the meal, pound for pound. Hence, any increase in oil yields enhances the possibility for greater earnings from the sale of products. It was natural, then, for the industry to adopt solvent extraction because of its larger oil yield. Solvent extraction came in rapidly after World War II, when oil prices nearly doubled, and growth was again accelerated by the Korean War influence on oil prices.

Mixed Trends in Industry

The industry has nearly always had excessive processing capacity, which causes great competition for the available seed supply (19). This was not particularly serious from the mill point of

view when the break-even point might be reached early in the season (16). (The break-even point is defined as the number of days a mill must operate to realize a gross income that will cover annual operating charges.) Under today's conditions, however, the break-even point is reached at a later date.

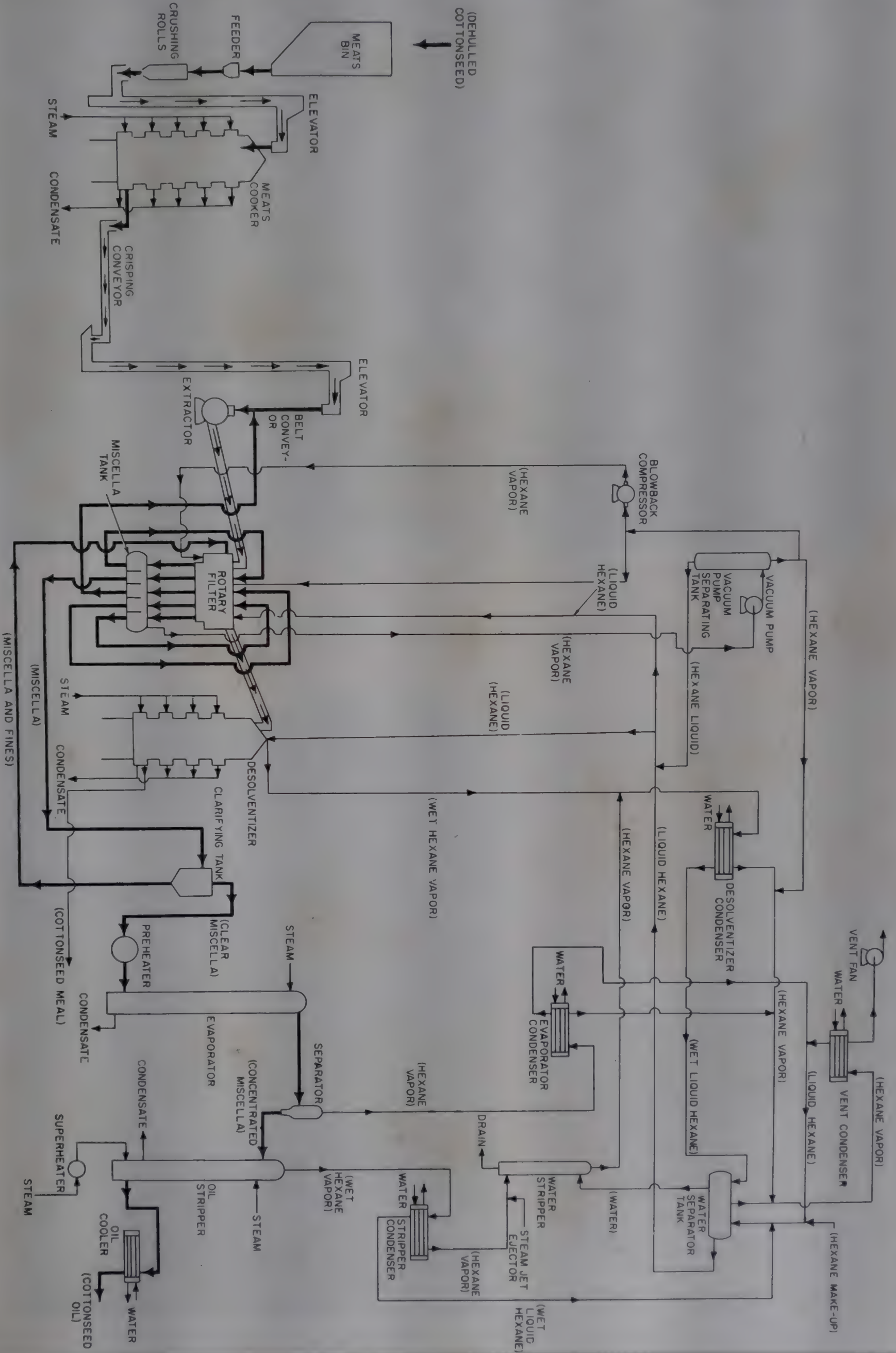
A trend toward larger mills makes the situation more complex. To modernize his mill and boost its daily capacity, a mill owner must be assured of the availability of enough raw material in his location or the possibility for bringing it in at a reasonable cost.

New developments in mechanical screw pressing—higher shaft speeds and extended pressing cages—have made it possible to increase the capacity of individual units or boost oil yields. Meanwhile, solvent-extraction processes have also enjoyed technical improvements—filtration-extraction and more compact, packaged units. Both are designed to make the small- or medium-sized plant efficient as well as economical to operate. Technological advances in screw pressing and solvent extraction—aided by lower equipment costs and design improvements that have reduced installation costs—have produced intense competition between these processes for new or converted installations.

Today the cottonseed oil mill operator



The filtration-extraction plant of Mississippi Cottonseed Products Co., located at Greenwood, Miss., processes from 140 to 200 tons of cottonseed per day or 80 to 130 tons of soybeans. On the opposite page, an artist's sketch of the plant



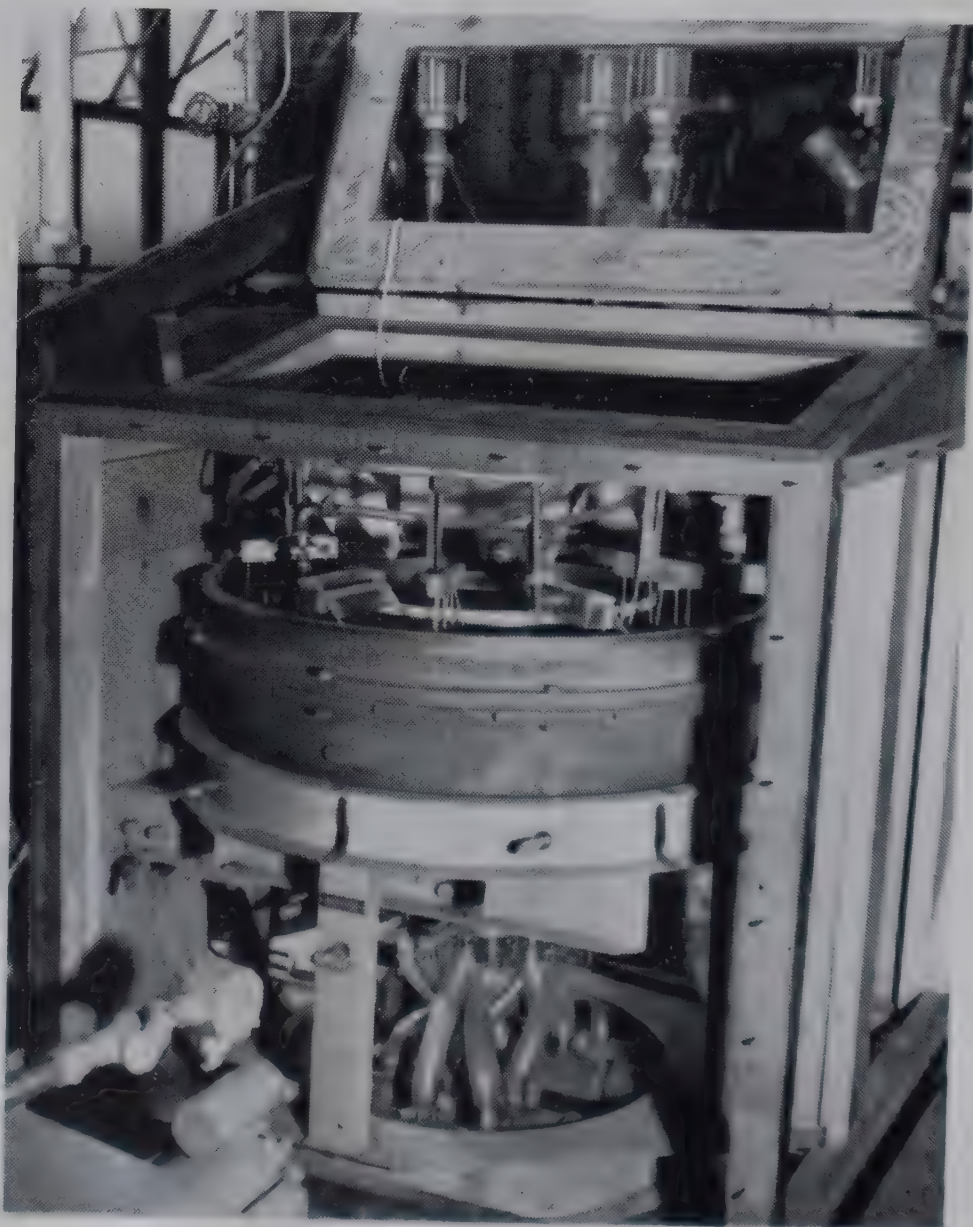


Feed conveyor and variable speed drive used by USDA in pilot-plant development work

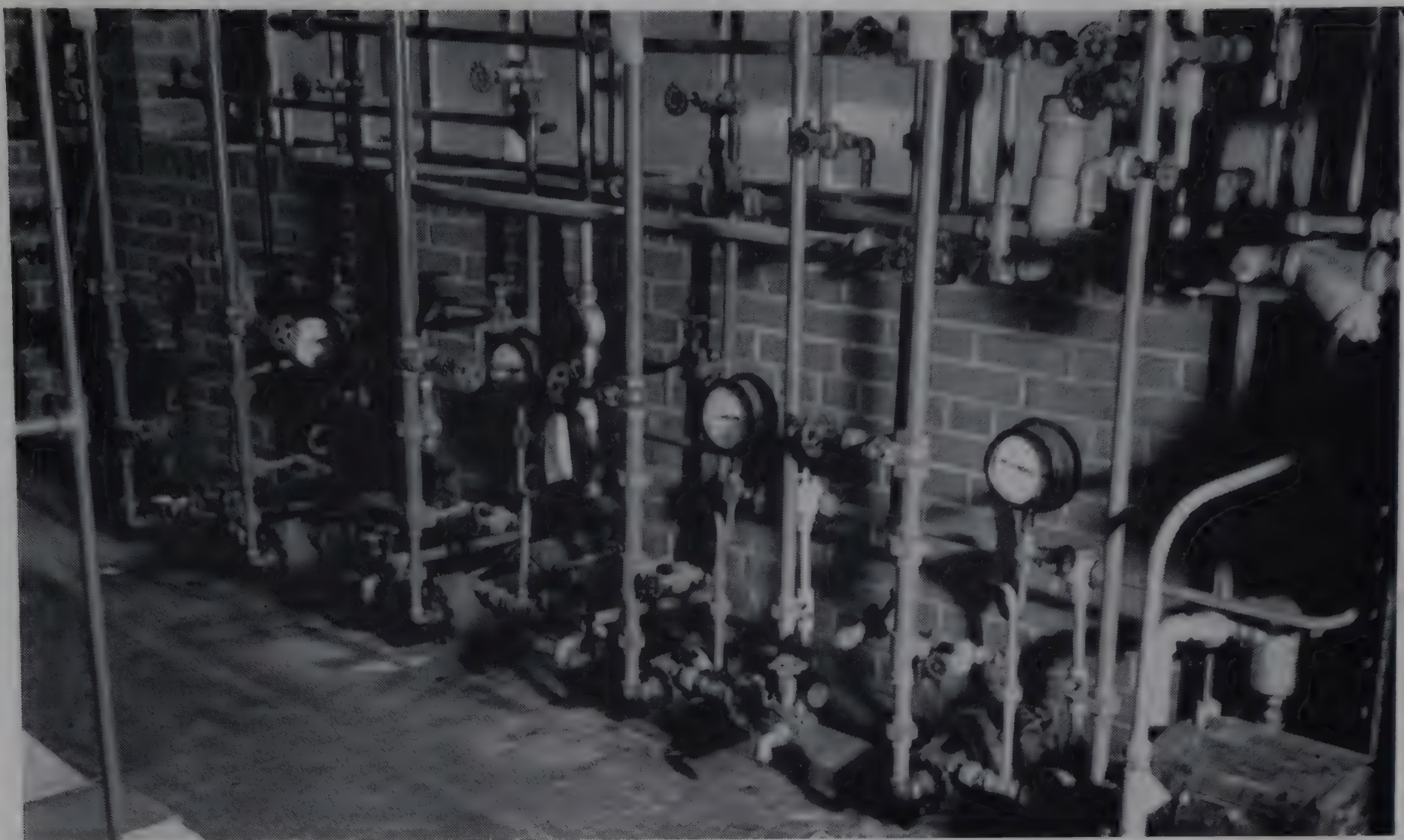
may choose among many methods which include—hydraulic pressing; screw pressing, at regular speeds, at high speeds, or with extension cages; direct solvent extraction; or prepress solvent extraction. The solvent-extraction phase of the last two methods may be conducted in many kinds of equipment—vertical column; vertical basket; rectangular basket; horizontal basket; filtration-extraction; horizontal rotary compartment; horizontal in-line compartment; horizontal traveling belt; or U-tube screw conveyor.

In recent years, attempts were made by several small operators to use trichloroethylene as a solvent in place of hexane because of its lower flammability. However, soon afterward, some of these processors learned they were producing a meal which was toxic to livestock. Also, one processor experienced a serious welding accident because he thought trichloroethylene was completely nonflammable. Since then, these processors have switched back to hexane, which the industry appears to have adopted exclusively. Yet the long range need still exists for nonflammable solvents that are inexpensive and nontoxic.

Early soybean mills used screw presses. When soybeans moved into the South some cottonseed oil mills (hydraulic) began to process this crop. But the flakes are a "natural" material for solvent extraction (20), and in recent years solvent



Small-scale horizontal, rotary vacuum filter used in USDA pilot-plant work



Filtrate pumps employed in USDA pilot plant

extraction has almost entirely replaced screw pressing as the primary method of recovering soybean oil. However, when the spread between product values and bean prices is small, it is difficult even to justify solvent extraction (15). Similar conditions could some day occur in the cottonseed industry that would force screw pressing into obsolescence.

Mechanical vs. Solvent Extraction

Today the larger hydraulic mills are converting to solvent extraction at an increasing rate. This is not surprising because these larger mills are situated in areas that afford enough seed to enable the mills to operate for 300 or more days per year. Larger mills usually have sufficient storage capacity to keep their operations running for this length of time.

Smaller mills normally have enough installed capacity to press from 60 to 100 tons of cottonseed per day. But they operate for 5 or 6 months per year, depending upon the size of the available crop. Small mills (rated by annual tonnage crushed) depend more upon an excess of installed capacity to handle their supplies of seed rather than upon storage of seed for a longer crushing season.

Then, this is why hydraulic pressing was the backbone of the industry for so long. Plant equipment was rugged and had a long life. It could be operated satisfactorily by semiskilled labor. Technological problems involved in the

production of salable products were well understood—it was usually possible to manufacture high quality oil and acceptable meal from seed of widely varying quality from all portions of the cottonseed producing area.

As long as costs remained low—the principal item being labor—the incentive for technological improvement was largely that of increasing oil yields. It is likely that every oil mill superintendent who ever worried about his daily problems, conducted within the limits of the facilities at hand some kind of mill-scale testing aimed at boosting oil yields. But progress was slow. Today the average oil content of hydraulic press cake probably ranges from 4.0 to 5.0%.

Over the past two decades screw pressing has been improved considerably. The residual oil in screw-press cake today will probably average between 3.0 and 4.0%, even though results below 3.0% are occasionally reported. To achieve optimum results it is necessary to cook and condition cottonseed meats to a much lower moisture content (2 to 4%) than is best for hydraulic pressing (5 to 7%), and somewhat higher cooking temperatures are normally used. If this is not done, high throughput and low residual oil content, upon which economical and efficient operation of the screw press depends, is not achieved.

Screw pressing is a more sensitive operation than hydraulic pressing. It requires experienced help, and the presses themselves must be kept in the best of mechanical condition to achieve continuous high efficiency.

In screw pressing, temperature of the cake rises as the cake passes through the press. Because of the high pressures developed, temperatures high enough to cause darkening and plastic flow are sometimes observed. This is in contrast to hydraulic pressing, where cake temperatures show a significant drop during pressing operations. The difference in pressing temperature is probably the major explanation for the difference in residual oil content obtained by the two methods.

Satisfactory operation of a group of screw presses is complicated by the necessity for remixing the settlings or "foots" from the pressed oil with the cooked meats being fed to the screw presses. It is not always possible to feed this material uniformly throughout each hour of the day. There is some tendency for the material to segregate in conveyors and feed disproportionately so that one press will receive more "foots" than another.

Compared with hydraulic pressing, the principal advantages of screw pressing are higher oil yield, greater capacity, and lower labor cost. It has the disadvantages of increased power consumption, installation costs, and maintenance costs.

Direct solvent extraction has now been developed at some mills to an efficient operation producing a residual oil content in the extracted meal of only about 1%. However, to obtain high extraction efficiency, much attention must be given to preparation operations. Removal of fines from the miscella becomes

serious if proper preparation is not used.

Direct solvent extraction boosts oil yields. Oil is the most valuable product of oil milling. If the plant is large enough and can be operated for about 300 days per year, over-all costs, including labor, are lower. But solvent-extraction plants are expensive; they require well trained operators to obtain high extraction efficiencies and to maintain safe operating conditions.

In 1949, prepressing ahead of solvent extraction was introduced. Results so far indicate that prepressing solves many of the serious and immediate problems associated with direct solvent extraction and further increases oil yields. Solvent losses are lower; safety is improved. Prepressing increases considerably the capacity of any given size of extraction plant mainly because there is less oil to extract and the rate of extraction of the better formed flakes is increased greatly by the preliminary preparation, cooking, prepressing, and reforming. Practically all operating costs except power are reduced.

All processes for cottonseed utilize cooking (9), except direct extraction. Rolling and cooking before mechanical extraction has numerous advantages. It greatly increases pressing capacity, reduces power requirements, and improves both oil and meal quality. Cooking also eliminates differences in processing characteristics from one cottonseed lot to another; moisture adjustment during cooking lessens the difficulties imposed by varying moisture contents of raw cottonseed. Moreover, when cooking is used the extracted meal product comes out with a rich, golden-brown color.

In screw-press and prepress-solvent plants, the material after cooking must be dried to reduce moisture to a relatively low level. Otherwise, the presses will not operate properly. Cooked material is dried either in the lower ring of a stack cooker or in separate equipment. This operation may involve an increase in the temperature of the meats up to 250° F.

Prepress-solvent extraction recovers more oil than other processes. About three-fourths of the oil is removed by the presses, leaving about 10% in the cake to be removed by solvent extraction. Prior to extraction, the cake is usually moistened (9 to 10% water), then conditioned at 140° to 150° F., and passed through smooth flaking rolls for extraction.

Filtration-extraction process differs from the direct and prepress extractions in that it uses a slurring step (temperature, 125° to 135° F. and 30 to 45 minutes) to replace the usual counter-current diffusion-extraction, employed by other extraction processes.

PROCESS ADVANTAGES

- ▶ Extraction to a residual oil content of 1% or less
- ▶ Final miscella refiltered to low fines content on a continuous filter—refiltration and continuous settling eliminates the need for a polishing filter
- ▶ Preparation steps involve normal types of rolling and cooking equipment conducive to production of high quality products. Cottonseed oil quality is uniformly high even with exhaustive extraction
- ▶ Solvent content of marc is exceptionally low
- ▶ Oil content of final miscella is high
- ▶ Low solvent requirements give greater capacity in the recovery equipment at low steam consumption
- ▶ Solvent losses are low
- ▶ Process can be placed on stream in several hours—operators can change from one oilseed to another without a shutdown and with minimum interim mixing of products
- ▶ The process is versatile; it can handle most oilseeds
- ▶ Prepressing is not required, even for high oil content materials
- ▶ The filter is slow-moving; its accessories have many self-regulating features
- ▶ Process has a high capacity for small filter units
- ▶ It is an integrated process that requires a minimum of attention—one operator per shift
- ▶ Lower installation cost in comparison with other processes
- ▶ Low power requirements and low maintenance costs

Filtration-Extraction at Greenwood, Miss.

The filtration-extraction plant of the Mississippi Cottonseed Products Co., located at Greenwood, Miss., has been essentially in continuous operation on cottonseed and soybeans since January 26, 1954. It processes from 140 to 200 tons of cottonseed per day (or 80 to 130 tons of soybeans). This plant was designed, constructed, and erected by Lukenweld Division of Lukens Steel Co., based on the initial bench-scale (47) and pilot-plant development (3, 4, 13, 18, 25, 32) work and patents (2, 21, 22, 27, 38, 39) of the Southern Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture. Active co-operation was maintained between the Lukenweld Division, Lukens Steel Co., and Mississippi Cottonseed Products Co. throughout all phases of the project, including initial operations on cottonseed and soybeans.

The success achieved in this first installation has led Mississippi Cottonseed Products Co. to construct a second plant at Hollandale, Miss., of about the same size and for the same raw materials (10). Wurster & Sanger, Inc., Chicago, Ill., engineered the Hollandale unit. (This company recently acquired the right to Lukenweld Division of Lukens' process know-how.)

Various estimates have been prepared on the cost of filtration-extraction plants (1, 6, 23, 33, 34), which range from

\$300,000 upward for a unit processing 100 tons of cottonseed per day.

Rolling, Cooking, and Crisping. Proper preparation is necessary if the raw material is to have good extractability (37) and filterability, a reasonable minimum fines content, and proper size distribution (5, 11, 17). Filterability is enhanced by preparing a material that is relatively incompressible.

Cottonseed and soybeans are both hulled. Subsequent operations are more efficient and more uniform when the hulls are more completely removed, and equipment capacity is increased. However, some or all of the hulls may be added to the meats prior to extraction, or after, to lower or control protein content of the final meal product; when soybeans are being processed, any hulls so used should be returned to the meal products after solvent extraction.

Cottonseed meats and cracked soybeans are conditioned to make the rolling operation more efficient. For both, a temperature and moisture content is used that will not quite produce a plastic flake. This promotes oil release (but

For detailed cost analysis, see "Filtration-Extraction Process. Cost Analysis Application," by K. M. Decossas, H. G. Many, O. J. McMillan, Jr., E. A. Gastrock, and E. F. Pollard, Ind. Eng. Chem. 49, 930 (1957)

Operating Sequence of Solvent Extraction Processes (12)

(Time in minutes, including conveying time)

Unit Operation	Extraction		
	Filtration	Direct	Prepress
	Preparation		
Meats conditioning	3	3-20	3
Multipass rolling	2	...	2
Cooking	24-36	...	15-45
Drying	{15-30}	...	20-40
Cooling	
Prepressing	3
Grinding	3
Conditioning	10-15
Flaking	...	2	2
Total	44-71	5-22	58-113
	Solvent Extraction		
Premixing or slurring	30-45
Countercurrent diffusion-extraction	...	45-60	30-50
Countercurrent filter washing	1-3
Marc drainage			
Gravity	...	^a	^a
Squeezing	...	^b	^b
Suction
Total	31-48	45-60	30-50

^a Included under diffusion-extraction.^b Included under diffusion-extraction (employed to a limited extent).^c Included under countercurrent filter washing.

not actual oil flow), although it consumes slightly more power than if the operation was conducted in the plastic range. Optimum moisture content for flaking is proportional to the oil-free, moisture-free meal content of the raw material. Temperatures range from about 140° to about 170° F.

Adequate rolling capacity cannot be overemphasized. Five high, heavy-duty rolls are best for processing cottonseed, and one pair high flaking rolls are satisfactory for soybeans. With cottonseed, rolling weakens or ruptures the pigment glands so that the free gossypol may be bound during the cooking operation, thus producing better quality oil and meal (20). During rolling for filtration-extraction, fines need not be avoided because the cooking operation consolidates the material in a later step. When conducted properly, rolling produces a balanced screen analysis that will provide adequate oil release, rapid extraction, and good washing and drainage on the filter.

Multipass rolling is of prime importance in filtration-extraction, prepress extraction, and mechanical extraction, where cooking follows rolling (29). But multipass rolling is not desirable for direct solvent extraction of uncooked flakes, because it produces a great amount of fines.

Prepared cottonseed or soybean flakes are cooked in conventional four-to six-high stack cookers, at somewhat lower temperatures and shorter cooking times than normally used for hydraulic cooking of cottonseed. Maximum temperatures normally do not exceed 225° F. The cooking time is short for soybeans (25 to 40 minutes), whereas longer

times are needed to prepare cottonseed (40 to 75 minutes).

Moisture content of the material throughout the cooking period is maintained at levels between 12 and 20%, which are higher than those employed for cooking that precedes hydraulic pressing. Optimum moisture levels depend on many variables, including oil content, protein content, protein solubility, and other characteristics of the material.

The cooking step, an innovation for solvent processing of soybeans, is essential to the filtration-extraction process. It produces a material with the characteristics needed to promote rapid oil extraction and easy drainage of liquids on the filter. Cooking has a twofold function—to complete the oil release started during conditioning and rolling, and to agglomerate the fines.

Under selected conditions, rapid reduction of the free gossypol content of the meal to recommended levels (0.03% or less) can be accomplished during cooking. Under these conditions the oil produced also has a relatively low gossypol content, making it much less susceptible to color reversion during storage. With properly conditioned and multipass rolled meats, cooking time can be shortened, producing at the same time meals of relatively high nutritional value.

The material after cooking is then crisped to "fix" the porosity of the particles. During this operation, 1 to 3% of water is purposely lost by evaporative cooling in the conveying operation that follows cooking. Crisping gives the cooked particles their relative incompressibility needed for filtration rates that result in higher filtration capacities.

It promotes oil extraction and filter drainage, and lessens the quantity of fines.

Each particle, after crisping, appears to be separate from the other; a handful when pressed together can be easily separated. Final moisture content after crisping is held within a range of 7 to 11%. The optimum level is 9%. Evaporative cooling, besides lowering temperature (to about 140° to 150° F.), simultaneously reduces moisture to the proper level for good extraction efficiency.

Filtration-Extraction. Extraction begins with the slurring step, where oil is put into solution at the highest possible concentration by mixing the crisped material with one of the miscella filtrates. This filtrate may contain initially about 9 to 12% oil and the balance hexane, depending upon operating conditions. During the slurring step, the oil concentration often increases to 25% or more.

The slurry mixer, or extractor, is a mildly agitated, horizontal tank (8E9), which holds the slurry for 30 to 45 minutes at temperatures between 125° and 135° F. When either cottonseed or soybeans are being processed, the solvent-to-feed ratio is maintained between 1.1 and 1.2 to 1, which gives a solids concentration of about 30 to 35% in the extractor. At Greenwood, the extractor was designed for maximum mixing with minimum reduction of particle size; progressive movement of material through the extractor prevents short circuiting.

This slurry is filtered on a commercially available horizontal, rotary vacuum unit (4E7), 10 feet in diameter, which contains five compartments. The filter performs four functions.

► It separates miscella from solids in the slurry.

► It refilters the most concentrated, or product, miscella to reduce the fines content.

► It provides an effective, three-stage countercurrent washing operation in which oil-free hexane is used as the final wash. (The first and second washes are made with weak miscellas containing 1 to 3% and 0.3 to 0.6% of oil, respectively.)

► It reduces the solvent content of extracted and washed marc to a very low value (25 to 30%).

Total time on the filter has been calculated as between 1.5 and 4.5 minutes. (Speed of rotation is varied to get optimum bed depth.) The filter operates continuously and automatically; even distribution of material is aided by a blowback (6E7) that continuously clears the screen of meal particles. The filter is equipped with a 60- × 60-mesh square weave stainless steel screen that has an average life of about 10,000 tons of cottonseed. It operates at reduced pres-

Comparison of Oil and Meal from Different Processes (21)

	Extraction			Pressing	
	Filtration	Direct	Prepress	Screw	Hydraulic
Gossypol in oil, %	0.01-0.05	0.1-0.2	0.15-0.4 ^a	0.05-0.3	0.03-0.10
Free gossypol in meal, %	0.03-0.07	0.20-0.40 ^b	0.03-0.08	0.02-0.08	0.09-0.30
Residual oil in meal, %	0.5-1.5	0.5-1.5	0.4-1.5	2.8-4.0	4.0-5.0
Alkali solubility of meal, % ^c	55-70	70-83	60-80	35-65	55-75

^a Prepressed oil, 0.2-0.5%; solvent-extracted oil, 0.05-0.20%.

^b 0.03-0.06% for chemically degossypolized meal.

^c Solubility in 0.02N sodium hydroxide.

tures of up to 10 inches of mercury (43).

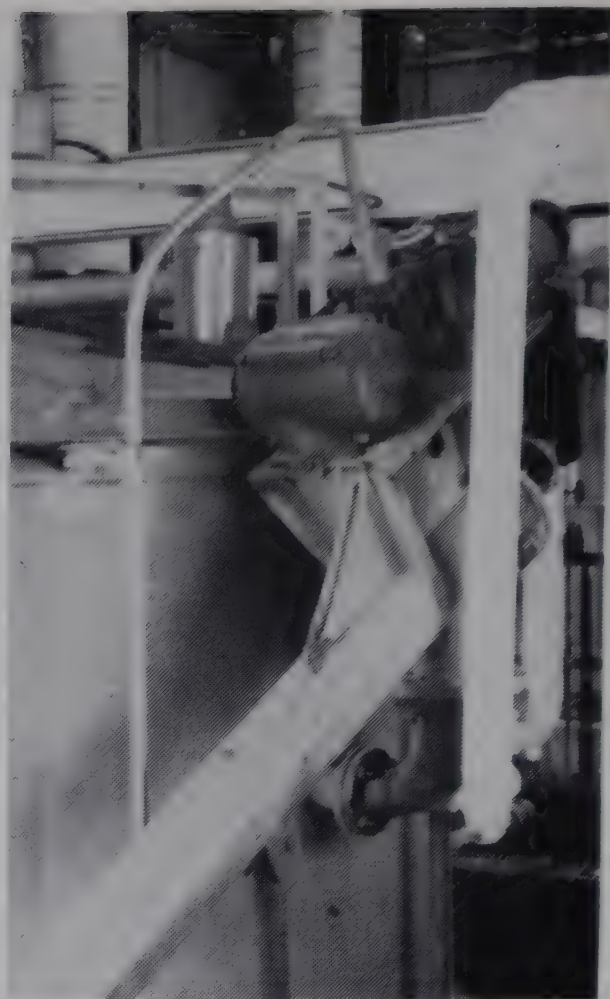
Enclosed conveyors (8E3, 8E5) move the slurry to the filter and remove the marc from the filter. The marc is elevated (8E8) and conveyed (8E6) to a desolventizer (3E). Cottonseed meal leaves the desolventizer in a conveyor (8E4), where it is elevated (7E) to a final cooler conveyor (8E7).

Final miscella from the compartmented miscella tank (8E10) is pumped (4E2) to a cone-bottomed clarifying tank for continuous removal of fines. The clear miscella goes to an evaporator (5E4) after it is preheated (5E5). Concentrated miscella leaving the evaporator-separator (8E12) flows to a steam-heated vacuum oil stripper (8E1) where hexane is recovered from oil with live superheated steam. The fin-

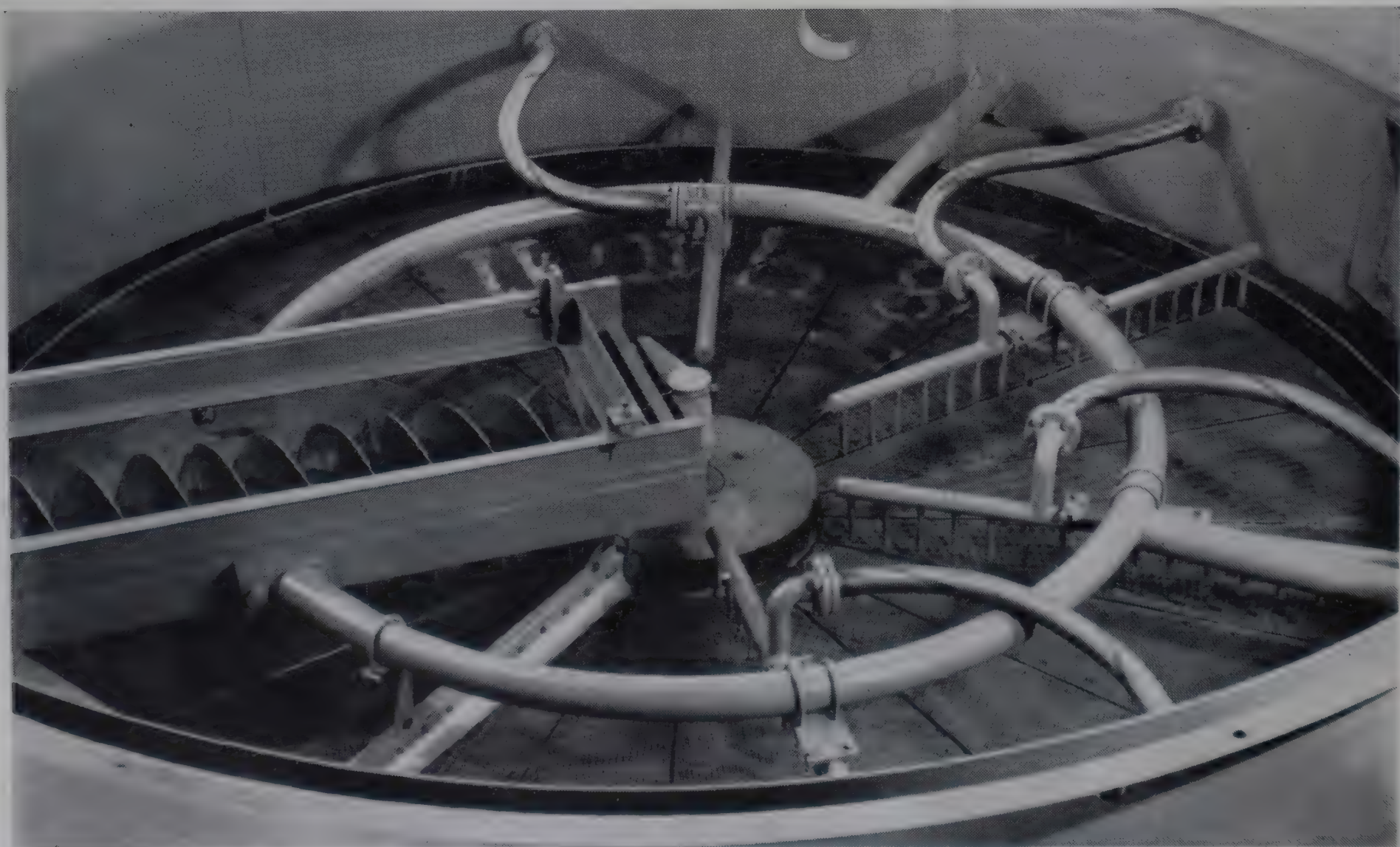
ished product is pumped (10E) to a cooler (2E) and sent to storage.

The evaporator and oil stripper are both equipped with condensers that liquefy the solvent. Hexane leaving the stripper condenser (5E1) contains water that was injected as live steam into the stripper; this stream goes to a water separator tank (8E13) where hexane make-up is added (1E2) from a solvent-storage tank (8E14).

Hexane vapors from the evaporator-condenser (5E3), the desolventizer-condenser (5E2), the vacuum pump (6E2), separating tank (8E11), and the water separator tank go to a common vent condenser (5E1) similar to the stripper condenser that is cooled by refrigerated water (1E1). Gases from this condenser are exhausted to the atmosphere through a vent fan (9E).



Slurry from the extractor moves by this conveyor to the horizontal, rotary vacuum filter



This is a close-up view of the horizontal, rotary vacuum filter (with vapor-tight hood removed) showing the wash nozzles, discharge scroll, and wash pan

Material Balance for a 100-Ton-per-Day Cottonseed Processing Plant (14)

Stream	Pounds				
	Extraction			Pressing	
	Filtration	Direct	Prepress	Screw	Hydraulic
Cottonseed ^a	200,000	200,000	200,000	200,000	200,000
Linters ^b	19,000	19,000	19,000	19,000	19,000
Loss	12,230	12,230	12,230	12,230	12,230
Hulls ^c	44,420	44,420	44,160	47,340	48,400
Meat fraction	124,350	124,350	124,610	121,430	120,370
Oil in meats	36,830	36,830	36,830	36,830	36,830
Oil recovered by pressing	27,080	33,030	31,970
Press cake	97,530	88,400	88,400
Oil in press cake	9,750	3,800	4,860
Final meal ^d	88,400	88,400	88,400	88,400	88,400
Oil in final meal	880	880	620	3,800	4,860
Solvent in marc	29,470	88,400	58,930
Oil extracted	35,950	35,950	9,130
Total oil recovered	35,950	35,950	36,210	33,030	31,970
Miscella to evaporator	143,800	179,750	45,650
Miscella to stripper	39,940	39,940	10,140
Solvent from evaporator	103,860	139,810	35,510
Solvent from stripper	3,990	3,990	1,010
Total solvent in miscella	107,850	143,800	36,520
Total solvent	137,320	232,200	95,450
Solvent-meats ratio	1.10	1.87	0.77

^a 18.6% oil, 3.76% NH₃.^b 0.61% oil.^c 0.53% oil.^d 41.0% protein.

Water collected in the solvent-recovery system flows from the water-separator tank (8E13) to a water stripper (8E2), where it is injected with steam to remove any hexane before discarding to drain. Hexane vapor overhead goes to the desolventizer-condenser.

In direct solvent extraction, solution of the oil and countercurrent washing take place in the same vessel. Conventional extractors do not utilize the solvent as efficiently as the rotary vacuum filter employed in filtration-extraction. They take a longer time to remove the oil, and they require a higher solvent-to-feed ratio for equal oil removal—hence, the miscella concentration is lower.

Residence time in direct and prepress extractors for the respective miscellas may be greater than for the solids. This is especially true for total-immersion extractors. Basket and compartment extractors have considerable extractor volume not occupied by either solids or liquids. The total volume of all units of extraction equipment (not including recovery equipment) is from two to six times greater for direct and prepress solvent extraction than for filtration-extraction.

In all three processes, efficient marc drainage is desirable to reduce residual

oil and solvent content of the meal. When more solvent is left in the extracted marc, the process must have larger meal dryers and the operation consumes more steam. Vacuum filtration, as used in the filtration-extraction process, removes practically all of the entrained solvent—considerably more than is removed by the other processes which depend on free drainage.

However, the use of vacuum with a volatile and flammable solvent like hexane presents problems of a special nature. It is difficult to seal wet-type vacuum pumps with water as the sealing liquid, without forming emulsions from small amounts of entrained vegetable oils. (These emulsions cause solvent losses in the water separating tank.) Engineers solved this problem by using solvent as the sealing liquid in the vacuum pumps (7).

At Greenwood, the Mississippi Cottonseed Products Co. produces a meal with 9.5 to 13% moisture and 0.5 to 1% residual lipides (17). Free gossypol content ranges from 0.03 to 0.07%. Cottonseed meal normally contains 40 to 42% protein; soybean meal, 45 to 50% protein. Solvent losses seldom exceed 0.65% by weight of material fed to the extractor.

Other Oilseeds Extracted

It would be difficult to predict the average size of the nation's cottonseed crop during the next decade. But the size of the crop does not seem to be increasing. However, given the impetus of a combination of favorable conditions, the cottonseed crop could increase substantially in any one year.

Three trends, though, are evident—westward movement of the crop; larger farm units; and larger per acre production (19).

Our soybean crop, on the other hand, continues to increase in acreage and quantity. There is a definite southward movement of this crop.

Peanuts as an oilseed crop have practically disappeared. Like cotton, peanut production could increase substantially over a short period of time if conditions were favorable.

Flax, tung, milo germ, and rice, while not of major importance in the South as oilseed crops or by-product sources of vegetable oils, are the mainstays of some oil mills and the No. 1 crop in some areas.

Castor and sesame have received much attention in some parts of the country. These crops could become important—castor because of its significance to national defense and its great potential for industrial use, and sesame if high per acre yields are obtained.

There are other plants, not yet cultivated commercially, such as jojoba and Chinese tallow, that could become important because of the interesting chemical and physical properties of their products. They have possible industrial applications.

Looking forward to the time when many other crops might be processed by filtration-extraction, the Southern Regional Research Laboratory, USDA, has carried out a great deal of development work on numerous oleaginous materials. Rice bran, flaxseed, peanuts, milo germ, sesame seed, and castor beans have been studied in bench-scale tests (24, 30, 36, 37, 40). Rice bran, flaxseed, and milo germ have been handled in the continuous, filtration-extraction pilot plant (25, 35).

Bench-scale tests (26) and pilot-plant data have been correlated with full-scale commercial operations. Now data can be translated reliably from one scale to another; researchers can test new materials with bench-scale operations only, to determine commercial feasibility.

Filtration-extraction, on a commercial scale in this country, has been applied only to cottonseed and soybeans. Elsewhere, other crops are being considered. A plant is now under construction in Chile for extraction of rice bran and sunflower seed. (The unit was designed by Wurster and Sanger, Inc.) In the future, more adaptations of this process can be expected for other oleaginous materials, especially those of high oil content, to which filtration-extraction is particularly applicable.

Last year, USDA researchers published data on a new process—solvent cooking—that combines cooking, crisping, and slurring in a single step (42). In this process, the raw, rolled cottonseed meats are mixed in the solvent,

Utility Requirements of a Filtration-Extraction Plant

(Cottonseed processing)

Utility	Per Ton
Electricity, kw.-hr.	18
Steam, pounds	400
Water, gallons at 75° F.	2300

together with the required amount of moisture (containing added chemicals). The slurry is processed in a combined low temperature heating and azeotropic distillation step which reduces the moisture content to an optimum value, after which it is drained and given three washes on a horizontal rotary vacuum filter.

Solvent cooking has three advantages over processes now in practice. It offers the possibility of combining three operations into a single step. Chemicals can be introduced as needed to promote free gossypol reduction and maintain a high alkali protein solubility in the solvent extracted meal. Agglomeration and extractability of the solvent-cooked cottonseed meats can be controlled satisfactorily. In time, solvent cooking may work its way out of the laboratory and become a commercial process.

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Processing Equipment

- (1E) Aurora Pump Co., 3017 Loucks St., Aurora, Ill., (1E1) centrifugal pump, 1.5 hp., 1750 r.p.m.; (1E2) centrifugal pump, 2 hp., 1750 r.p.m.
- (2E) Brown Fintube Co., 140 Huron St., Elyria, Ohio, four tube heat exchanger sections, 113 sq. ft. each.
- (3E) Davidson Kennedy Co., Atlanta, Ga., four hearth solvent recoverer, 84 X 30-inch hearths.
- (4E) Dorr-Oliver Inc., Stamford, Conn., (4E1) horizontal rotary filter, 65 sq. ft.; (4E2) centrifugal pump, 3 hp., 1750 r.p.m.
- (5E) Kewanee-Ross Corp., 1407 West Ave., Buffalo 13, N. Y., (5E1) condenser, 71 sq. ft.; (5E2) condenser, 291 sq. ft.; (5E3) condenser, 264 sq. ft.; (5E4) rising film evaporator, steam jacketed, 948 sq. ft.; (5E5) fintube preheater, 140 sq. ft.
- (6E) Nash Engineering Co., 300 Wilson Road, So. Norwalk, Conn., (6E1) compressor, 100 c.f.m., (6E2) compressor, 500 c.f.m.
- (7E) Screw Conveyor Corp., 704 Hoffman St., Hammond, Ind., elevator, 9-inch o.d. by 18 feet long.
- (8E) Southern Boiler & Tank Works, 1199 Thomas St., Memphis, Tenn., (8E1) stripping column, 12-inch o.d. by 2 feet long, 8-inch disk and 11.5-inch donut on 6-inch spacing; (8E2) stripping column, 16-inch o.d. by 49 inches long, 5-inch disk and 4-inch donut on 3-inch spacing; (8E3) ribbon conveyor, 6-inch o.d. by 12 feet long; (8E4) conveyor, 9-inch o.d. by 4 feet long; (8E5) conveyor, 9-inch o.d. by 7 feet 6 inches long; (8E6) conveyor, 9-inch o.d. by 13 feet long; (8E7) conveyor, 9-inch o.d. by 100 feet long; (8E8) elevator, 9-inch o.d. by 21 feet 6 inches long; (8E9) 2500-gallon extractor tank, 42-inch o.d. by 30 feet 6 inches long; (8E10) miscella tank, 42-inch o.d. by 10 feet long; (8E11) separator tank, 20-inch o.d. by 6 feet long; (8E12) separator tank, 3-feet o.d. by 7 feet long; (8E13) 105 gallon separator tank, 38-inch o.d. by 8 feet long; (8E14) 15,000-gallon storage tank, 10-feet o.d. by 26 feet long.
- (9E) Sturtevant Mill Co., 2 Harrison Sq., Boston 22, Mass., fan, 200 c.f.m.
- (10E) Viking Pump Co., Cedar Falls, Iowa, gear pump, 1 hp.

Process Licenses

- (1) Alden, Vern E., 33 N. LaSalle St., Chicago 2, Ill.
- (2) Blaw-Knox Construction Co., 930 Duquesne Way, Pittsburgh 22, Pa.
- (3) Day and Zimmerman, 1700 Sansom St., Philadelphia 3, Pa.
- (4) French Oil Mill Machinery Co., Piqua, Ohio.
- (5) Tears Engineers, 4617 Cole Ave., Dallas 5, Tex.
- (6) Wurster and Sanger, Inc., 5203 S. Kenwood Ave., Chicago 15, Ill.



Sulfuric Acid from Anhydrite

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Germany

THE process for making sulfuric acid from calcium sulfate rather than elemental sulfur, pyrites, or other raw material was developed technically in Germany. It owes its origin to World War I, when iron pyrites needed in acid making, then imported mainly from Spain, could no longer be brought to Germany.

Efforts were made to use the sulfur content of the sulfates (plentiful in many deposits, especially as gypsum or anhydrite) as a substitute raw material. In 1915 W. S. Mueller of Farbenfabriken Bayer Leverkusen investigated the decomposition of calcium sulfate with additives in the laboratory. A relatively small plant at Leverkusen was then built consisting of two small cement kilns. However, this could not be operated successfully. H. H. Kuhne joined Leverkusen in early 1916 and undertook to make the process work. In 1918, he overcame all the difficulties which had prevented the regular production of a sufficiently concentrated sulfur

dioxide gas and of good cement clinker. He perfected the working of the kilns when he set up the true formulas for Reactions 1 and 2 (page 1206). A mole ratio of only $1/2$ carbon to 1 calcium sulfate was required instead of 1 to 1 ratio recommended by Mueller. Working on this basis, the practical mole ratio required on a large scale was established and the plant made workable. H. H. Kuhne may thus claim to be the father of the anhydrite process. The Leverkusen plant, operated as a production unit until 1931, was closed on economic grounds because there was no source of anhydrite nearer than the Hartz District.

In the meantime, the process developed into general industrial use. At the end of the 1920's, Imperial Chemical Industries built a large-scale plant at Billingham, County Durham, England. There was assistance from Leverkusen in the early stages of operation. First, with one kiln, 150 and later, with two

kilns, more than 300 tons each of acid and clinker were produced daily from anhydrite containing approximately 90% calcium sulfate. Some details of the Billingham plant have been reported (2). Later, a plant was put into operation at Miramas, near Marseilles, France.

Germany's first large-scale anhydrite sulfuric acid plant was built at Wolfen by the former IG Farben combine. In the final plant, there were four kilns, each 70 meters long and 3.20 meters in diameter, which, through improved kiln operation and heat economy, achieved a 25% increase in yield. By the end of World War II, 500 tons of acid and clinker could be produced daily.

In recent years, modern and well-engineered plants have been built in Linz, Austria, and Whitehaven and Widnes, England. All known plants which are using or have used the process are given in Table I.

The use of anhydrite or gypsum as a



raw material for sulfuric acid is competitive with older processes in countries with limited or no domestic sulfur or pyrites deposits. A plant of this type involves a high capital investment and within its marketing area there must be a demand for portland cement. Even so, large present-day demands for sulfur and the dwindling of easily accessible reserves in sulfur-rich countries requires a careful study of alternative sources of this important raw material.

In earlier articles in this series, modern mining of sulfur, extraction of sulfur from sour gases, and contact production of sulfuric acid from sulfur, have been described (7, 9, 12). The portland cement process in one of the two largest and most modern individual cement plants in the world was also presented (6). Because production of sulfuric acid from anhydrite is a conventional process once a supply of sulfur dioxide is available, emphasis of this article is placed on the chemistry of sulfate decomposition and differences in cement-clinker production.

Theoretical Studies and Chemistry of Anhydrite Process

Scientists have studied the decomposition of calcium sulfate for over 50 years. The first significant publications appeared at about the turn of the century. Lunge, in 1903, was the first to suggest that calcium sulfate could be directly decomposed to sulfur dioxide by heating with clay in a shaft kiln, with cement clinker formed as a by-product (4). However, temperatures required were too high for that period.

In 1908, Hofman and Mostowitsch published studies showing the effect of temperature on speed of decomposition of calcium sulfate with additives (5). They found that, without additives, decomposition begins at 1200° C. and ends at 1400° C., with simultaneous melting. Additives such as iron pyrites, iron oxide, and lead oxide increase the speed

of decomposition at these temperatures. This speed depends on the quantity of added material and the action of the additives.

Other workers (17) investigating the reaction between calcium oxide and sulfur dioxide found that the reaction is completed in two stages:



They observed that equilibrium of a system with solid phases CaSO_4 - CaO - CaS and coexisting SO_2 and S_2 occurs at temperatures between 850° and 950° C.

Some years later, Schenck and Hammerschmidt published the equilibrium ratio of sulfur dioxide to elemental sulfur (SO_2 - S_2) and basic phases of calcium sulfide and sulfate for several temperatures at atmospheric pressures (10).

Figure 1, based on work in England, shows that the proportion of sulfur vapor in the gas atmosphere is greater for lower decomposition temperatures, and, at any given temperature, varies with total pressure of the system (2).

In 1932, Zawadski reported experimental work on the equilibrium pressures of the reaction:



including not only the decomposition of calcium sulfate but also the effect of sulfur trioxide on calcium oxide. Also examined were the reactions:



and

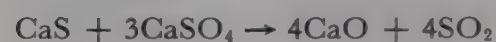


Table I. Plants Producing Sulfuric Acid from Calcium Sulfate

Location	Constructed in	Original Raw Material	Number of Kilns	Capacity and Remarks
Germany Leverkusen	1916	Gypsum; later anhydrite	1	40 tons per day. An experimental plant and later dismantled
Wolfen	1938	Anhydrite	4	85,000 tons annually increased to 200,000 by 1955
France Miramas	1937	Gypsum	1	25,000 tons per year. Operated until World War II. Operated again after the war but now shut down
England Billingham	1929	Anhydrite		100,000 tons per year increased to 175,000 in 1955
Widnes	1955	Anhydrite	2	150,000 tons per year
Whitehaven	1955	Anhydrite	2	100,000 tons per year
Poland Breslew	1950	Anhydrite		?
Busko				?
Zdroi				?
Austria Linz	1953	Anhydrite		45,000 to 50,000 tons per year

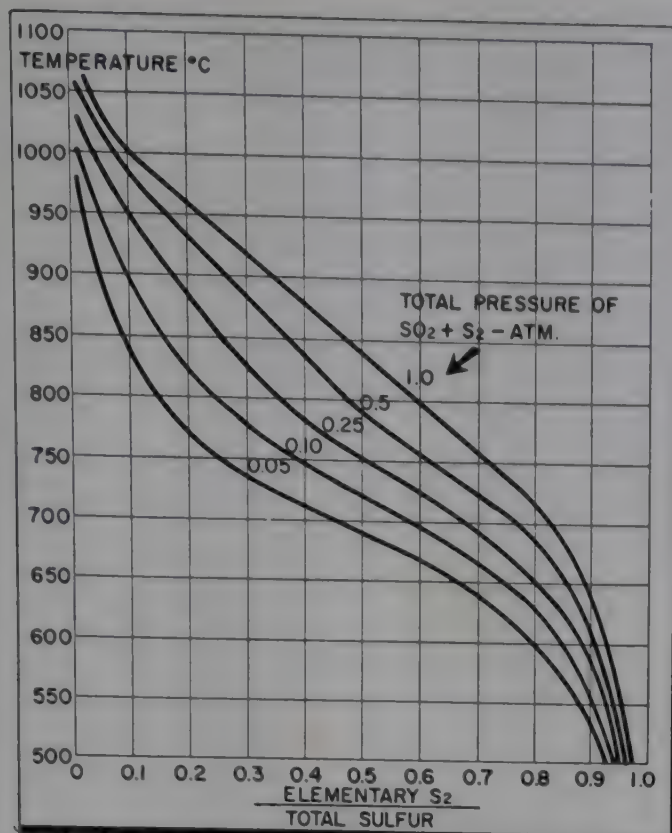


Figure 1. Effect of temperature and pressure on the amount of sulfur vapor in gas atmosphere (3)

The equilibrium pressures of sulfur dioxide and sulfur vapor were calculated by statistical and flowmeter measurements (14). The equilibrium pressures found agreed closely with those determined by other workers.

The decomposition pressures of calcium sulfate with various additives, such as iron pyrites, alumina, iron oxide, and kaolin at different temperatures have also been observed. Kaolin, in particular, has a significant effect on the speed of decomposition (8).

In more recent work, the effect of decomposition speed and dependence on temperature and additives, especially SiO_2 , R_2O_3 , particle size, and granular size with gypsum residues from the sulfate decomposition, have been investigated (13). Experimental studies of the effect of various coal or coke varieties, which are used as reducing agent in the industrial process, on the simultaneous production of sulfur were conducted at Imperial Chemical Industries' Billingham laboratory (2). Studies were made of the effects of temperature and grain size of the coal and coke varieties used. When various additives are used at a fixed temperature of 1100°C ., elemental sulfur is obtained:

Additive	% of Total Sulfur Content Evolved as Elemental Sulfur
Coke	15
Charcoal	30
Coal	50

Because of coal's high reducing characteristics and volatility, the reaction with it takes place at lower temperatures, resulting in an increase of elemental sulfur.

In the industrial anhydrite sulfuric acid process, coke is used as a reducing agent and enough aluminum-containing materials are added so that portland cement is produced ton-for-ton of acid.

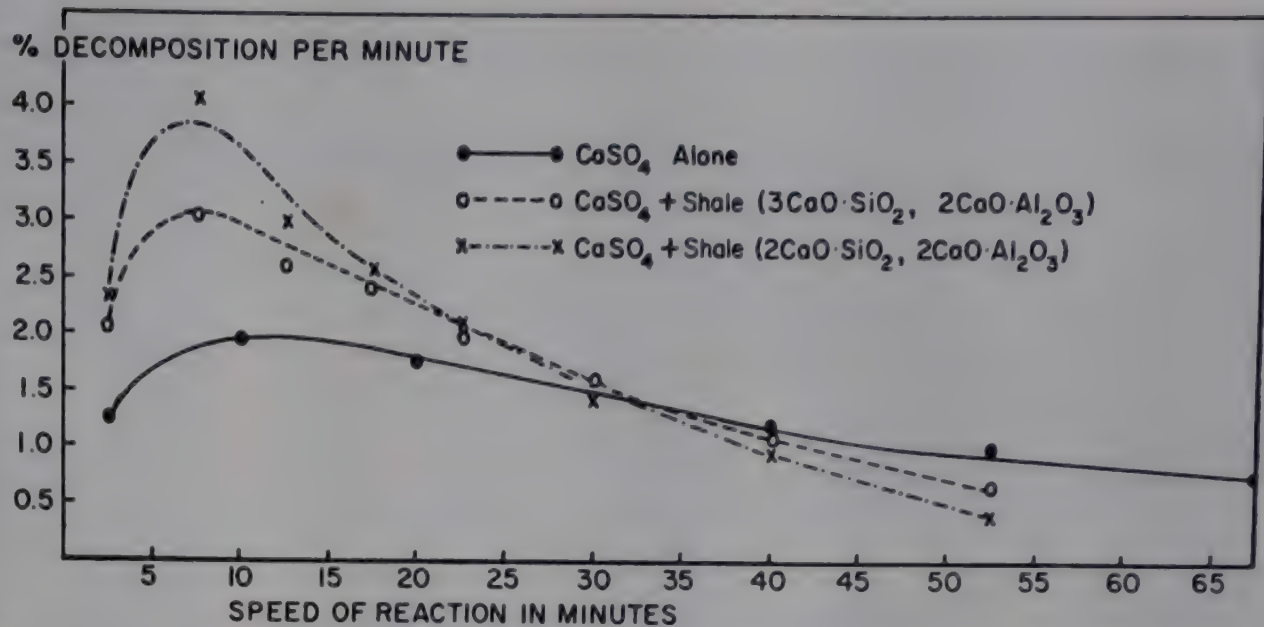


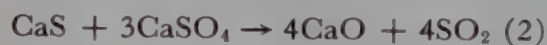
Figure 2. Speed of decomposition of calcium sulfate with shale as additive (work done at Wolfen)

Current knowledge of the dissociation of calcium sulfate under these conditions, to a great extent developed in Germany, indicates three stages:

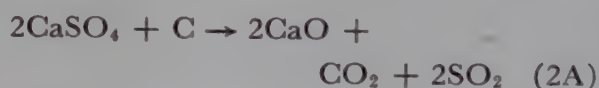
Stage 1. Reduction Step. Carbon reacts with a fourth of the anhydrite to form calcium sulfide:



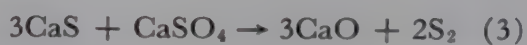
Stage 2. Decomposition Step. Calcium sulfide reacts with the remaining anhydrite at a considerably higher temperature to form sulfur dioxide:



Afterward, calcium sulfide exists only as an intermediate so that the over-all reduction course corresponds to the reaction:



Stage 3. Side Reaction. In a neutral atmosphere a side reaction occurs. Instead of sulfur dioxide, sulfur vapor is formed:



When coal is used, Reaction 1 takes place quantitatively in 1 hour. Coke is used industrially because of its low volatile content and low reactivity. In this case, reaction does not start until 900°C . and continues up to 1100°C .

Reaction 2, decomposition, has been much investigated. The calcium sulfide and calcium sulfate mixture has, at each temperature, a definite decomposition pressure of sulfur dioxide and sulfur vapor which reaches the partial pressure of 1 atm. at approximately 1200°C . Additives of clay or similar materials raise the decomposition pressure, so that at 1100°C . quantitative decomposition occurs in 1 hour. Components are present in the exact amount and ratio required for quantitative conversion. Too much calcium sulfide and calcium sulfate lowers the decomposition rate even at much higher temperatures.

As far as sulfur dioxide is concerned, this is the end of the process. The rest involves making of cement clinker. A further rise in temperature up to 1400°C . to 1450°C . completes the reaction between the components and lime, formed

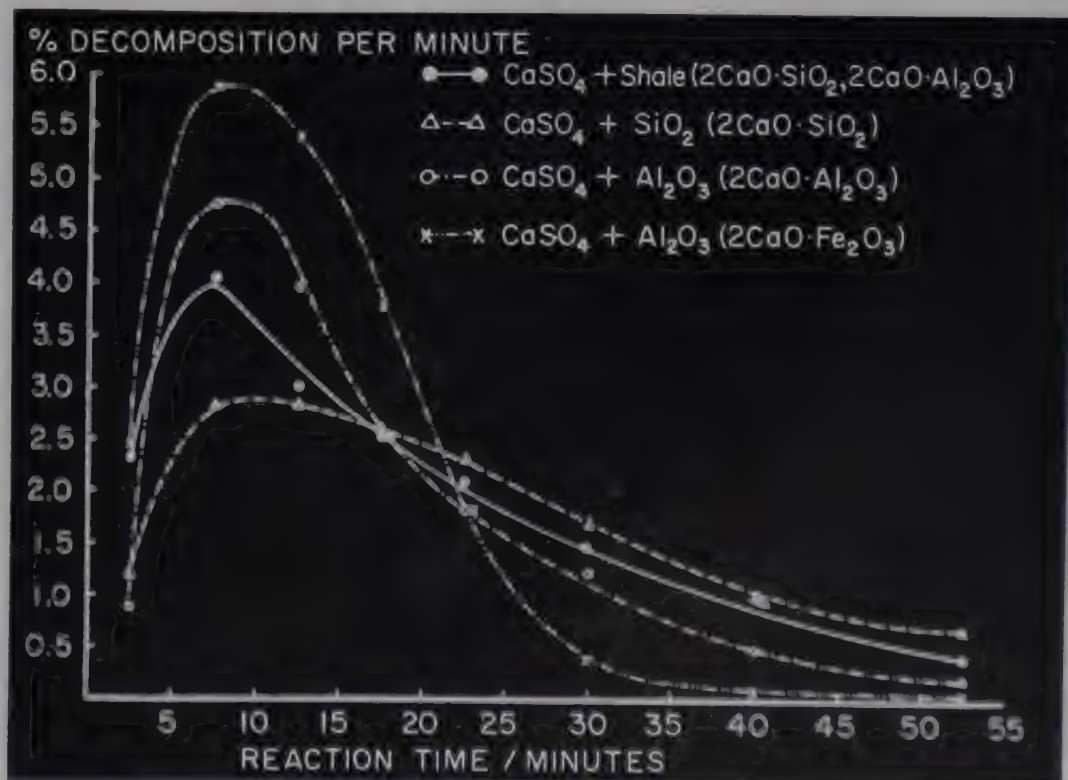


Figure 3. Decomposition of calcium sulfate at 1100°C . with various additives (work done at Wolfen)



Anhydrite is mined by pillar-and-stall method, headings being cut 18 to 20 feet wide and 12 feet high. Removal of about 60% of seam to its mined height is possible and no shoring is necessary. Each blast brings down about 70 tons and broken rock at the working surface is loaded by electrically-powered, track-mounted, over-throwing shovels into 3-ton Diesel dump trucks. Diesel-operated skid shovels are used for clean-up



From the underground storage hopper, anhydrite passes to the plate feeder immediately below which discharges to the first of a three-section conveyor which carries the rock up 3000 feet to the surface at a rate of 280 feet per minute



Dumpers discharge the anhydrite to the top of a 15-ton underground storage hopper through a grizzly with spacing of 10 inches. Oversized lumps are broken by grizzly attendant



From the drift, anhydrite goes over belt weighers to primary, and when necessary secondary crushing houses, final product being about $\frac{3}{4}$ inch. Mine labor receives a bonus based on total mine output

during decomposition, to produce a good clinker. In practice, decomposition and clinkering overlap.

Thorough investigations of the rate of decomposition with and without additives have been made. These were undertaken at both evenly rising and at constant temperatures.

Reactions 2 and 3 occur at 900° to 1000° C., in about the same order of magnitude. Higher temperatures strongly favor Reaction 2. If decomposition were to proceed exclusively according to Reaction 2, then it would correspond to the course of the over-all reaction. Reaction 2A, and 2B, make carbon would be needed per mole of

calcium sulfate. However, Reaction 3 proceeds with perceptible speed at calcium sulfate decomposition temperatures and, as shown by the reduction reaction, more carbon is consumed. At the same time, a certain formation of sulfur always occurs. If the decomposition leads to complete disappearance of calcium sulfate and calcium sulfide, the correct carbon content of the reaction mixture is being used. The quantity of carbon required for this, trimmed in accordance with the conditions in the rotary kiln, was obtained experimentally with 0.65 mole per mole of sulfur trioxide.

If additional materials are introduced to the reaction mixture to adjust the

lime evolved in Reaction 2, the dissociation pressure rises and speed of decomposition increases (Figure 2). The greater the amount of additive, the more the rate of decomposition rises. However, if an additive contains surplus calcium sulfate or surplus calcium sulfide it will be necessary to adjust the carbon content of the mixture. Surplus calcium sulfate requires more carbon for reduction; with surplus calcium sulfide, less carbon is required because some of the calcium sulfate will be decomposed by the calcium sulfide.

To determine which of the principal components of a clay additive—silicon dioxide, aluminum oxide, or ferric oxide

—most strongly influences decomposition, tests with clay compounds, as active oxides, were carried out (Figure 3). The amount of additive was so regulated that for 2 moles of calcium sulfate, 1 mole each of additive was used. At 1100° C., the following series results:

Slowest decomposition →
 SiO_2 , clay, Al_2O_3 , Fe_2O_3 →
 fastest decomposition

Besides an exact adjustment of the proportions of the reduction coke to the anhydrite, the proportions of the added materials to the calcium oxide and to each other must be carefully adjusted within determined limits, so that a good clinker results and, even more important, kiln operation can be carried out under steady conditions. Because of the special characteristics of the anhydrite process, a high lime content in additive components, which should be between 95 to 97%, is preferred to a high silicate and alumina content. The high lime saturation is useful: it helps the production of cement with high early strength.

Next in importance to the chemical reaction during calcium sulfate dissociation is the heat economy as compared with portland cement production. From viewpoint of the latter, only the calcium carbonate of the raw powder is replaced by anhydrite. However simple this substitution may appear, in large-scale production operations considerable differences are observed. It is striking that the clinker yield of similar kiln units is only half as large with the anhydrite process as when using a normal portland cement raw mixture.

These factors contribute to the markedly higher heat consumption:

The heat requirement for the dissociation is 64 kcal. for calcium sulfate and 38 kcal. for calcium carbonate.

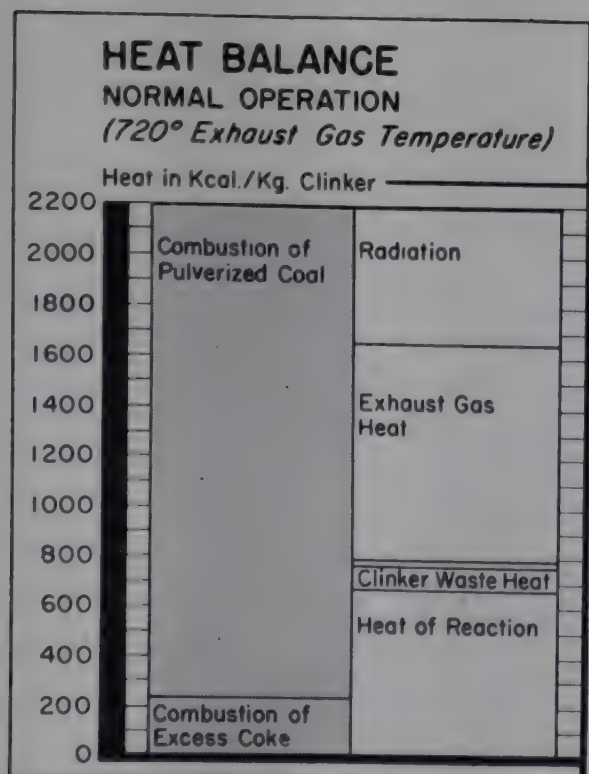


Figure 5. Heat balance at Wolfen plant before improvements in heat economy were introduced

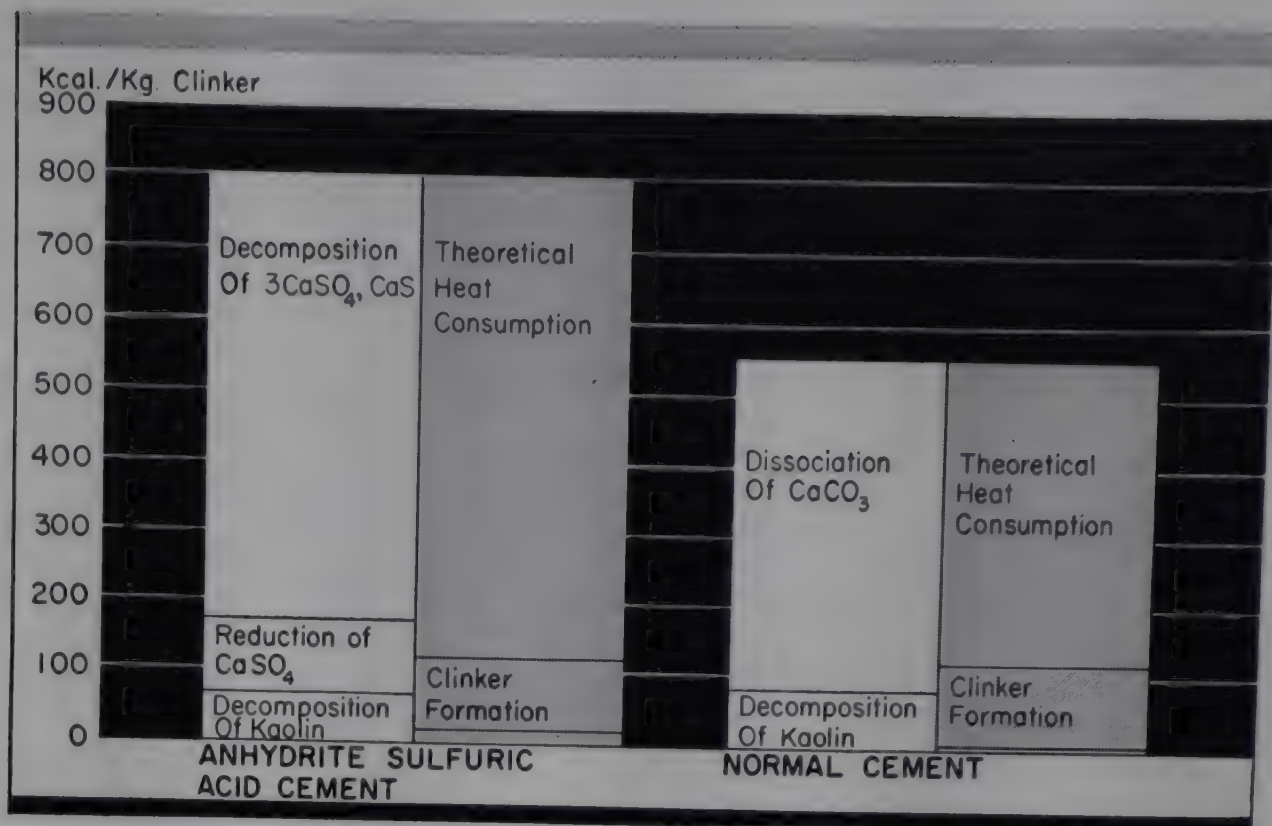


Figure 4. Heat consumption for clinker in anhydrite sulfuric acid process as compared with that of normal portland cement clinker

The roasting temperature required for decomposition of calcium sulfate starts at about 1200° C.; decomposition of calcium carbonate occurs at 800° to 900° C.

The utilization of waste heat in the kilns using the anhydrite process is still lower than that of the best kilns using the calcium carbonate process.

Figure 4 shows the difference in the theoretical heat consumption for one anhydrite acid clinker and one normal clinker. Figure 5 shows the original heat balance of the anhydrite sulfuric acid process before improvements in the heat economy were introduced in the Wolfen plant. From this the yield increases and improvements in heat economy, respectively, are promising, especially through better utilization of the waste heat and higher load of the kiln aggregates. The latter is a result of the lowering of the radiation losses per kilogram of clinker.

Owing to the high decomposition temperature, good results can also be obtained by use of a high value fuel yielding a hotter flame. Such fuel results in an increase of temperature difference be-

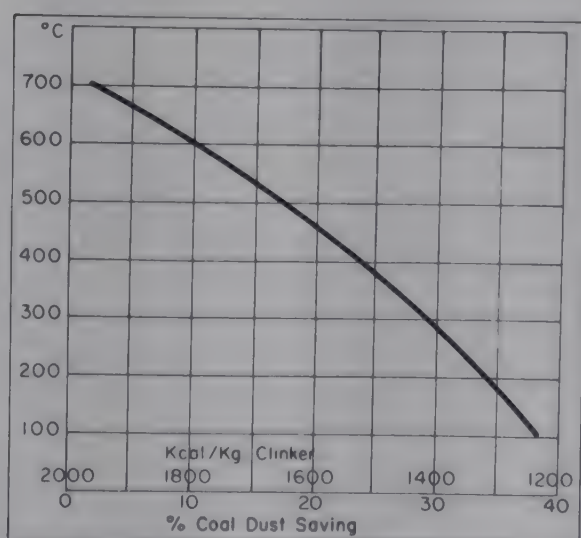


Figure 6. Saving of energy through lowering of waste gas temperature

tween flame and decomposition, heat transfer to the material is improved, and the discharge temperature is lowered. Discharge temperature is lowered through installations which provide an exchange of heat from the combustion gases to the material as it arrives.

Figure 6 shows how strongly the saving in energy is influenced by the lowering of the combustion gas temperature. There is a simultaneous corresponding rise in the sulfur dioxide in the gas (Figure 7). Cooling and power savings resulting from the lower temperature of the waste gases and lower gas quantity per kilogram of clinker, respectively, are some of the other advantages.

A further increase in yield in relation to the sulfuric acid produced can be achieved if the fuel coal is partially replaced by the burning of sulfur, or if sulfide is used in place of the reduction coke.

However, the clinker production, with the same production of sulfuric

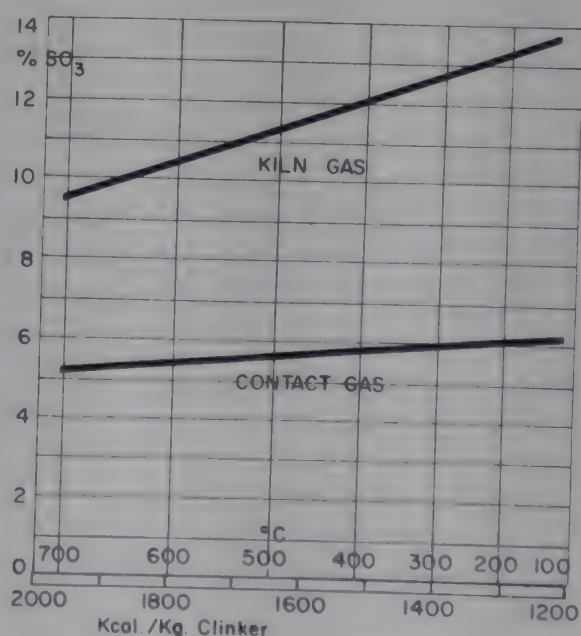


Figure 7. Rise in sulfur dioxide content of waste gas through lowering of waste gas temperature

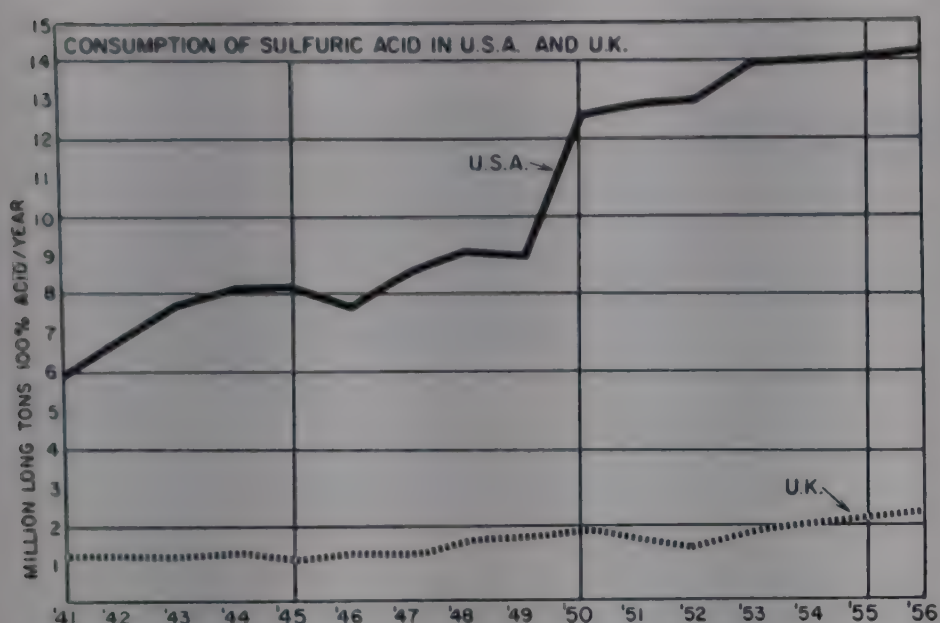


Figure 8. Sulfuric acid consumption

acid per kiln unit, can be increased by using lime-rich materials in place of clay, since the throughput of the kiln depends to a large extent on the amount of anhydrite.

Summarizing the theoretical introduction of the anhydrite sulfuric acid process, it is clear that a large number of conditions must be held within narrow limits and that only the combined working of all factors makes the satisfactory kiln operation possible.

Sulfuric Acid Requirements and Industry in U. K.

Sulfuric acid consumption in United Kingdom increased by 80% in the last 20 years (Figure 8). Immediately before the sulfur crisis in 1950, the principal raw material used was elemental sulfur imported in large quantities from the United States. Acid was also made from pyrites imported from Spain and other European countries. This latter

source was cut off during the war because of greater shipping space required by pyrites as compared with sulfur and isolation of principal sources of supply. As a result, nearly all new acid plants erected after 1940 and up to 1950 were sulfur-burning.

The sulfur crisis of 1950 caused a one third cut in U. K.'s sulfur imports from the U. S. Then the British government made a concentrated effort to develop other sources of sulfur for acid making. Large quantities of anhydrite of high purity exist in various parts of Northern England and use of this substituted raw material played an important role in the British government's £25,000,000 investment program in sulfuric acid plants. Figure 9 shows the increase in use of other sulfur-bearing materials by the sulfuric acid industry from 1951 through last year. In 1956, less than one third of the total U. K. output of sulfuric acid was made from elemental sulfur as compared with one half, 4 years earlier.

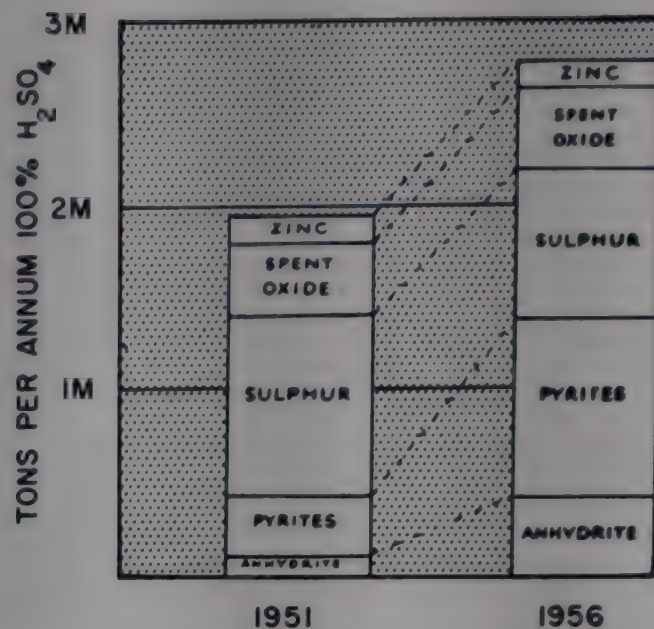


Figure 9. U. K. sulfuric acid capacity and raw material used

Marchon Products Ltd. Started as Small Detergent Producer

In 1939, on the Cumberland coast a mile or two south of the ancient port of Whitehaven, England, Marchon Products Ltd., built a small plant to make surface active agents and detergent intermediates. The company, 11 years later, had grown into an important chemical industry employing over 700 persons and had built up an extensive domestic and export trade in detergents and detergent raw materials.

As this plant was isolated from the principal sources of sulfuric acid, Marchon proposed an erection of a pyrites plant at Whitehaven when it became a large consumer of acid. The U. K. Board of Trade refused priority to construct another pyrites plant for at least 20 were already under construction as part of the general investment plan. Marchon, having found that its detergent plant was over one of the largest

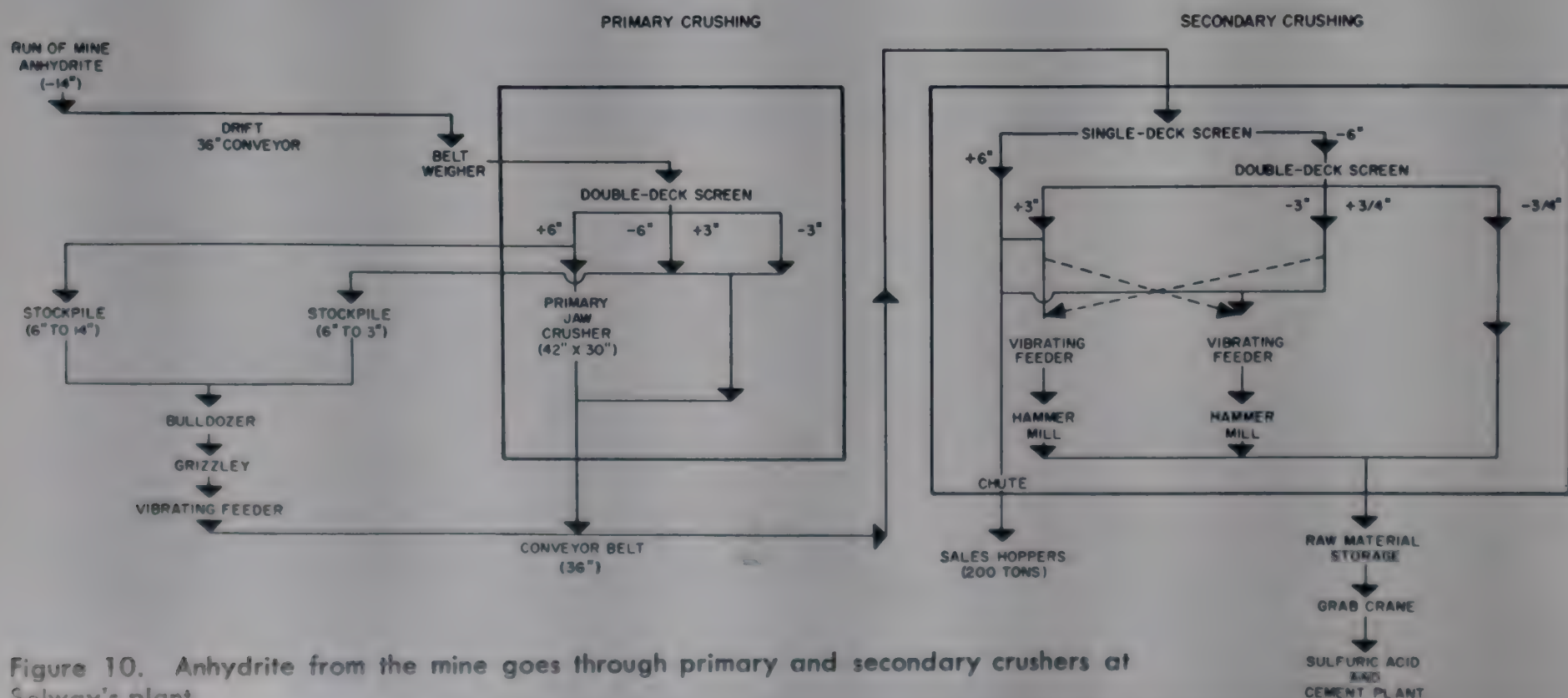
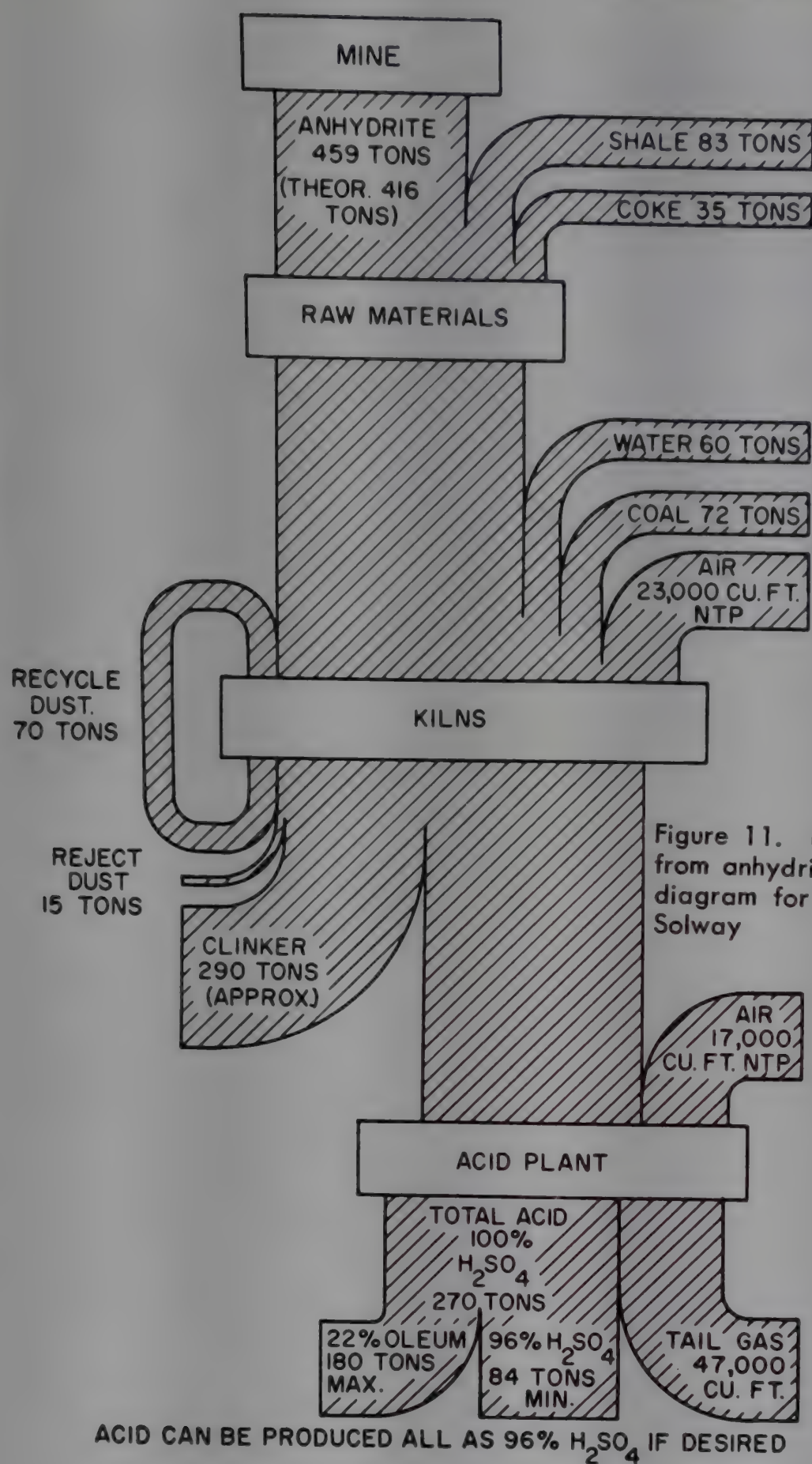


Figure 10. Anhydrite from the mine goes through primary and secondary crushers at Solway's plant



seams of anhydrite in Great Britain, thus considered calcium sulfate.

The fortunate plant location resulted in establishing a subsidiary company, Solway Chemicals Ltd., to erect a sulfuric acid plant using anhydrite as sulfur source. The U. K. government soon saw that Solway could make a substantial contribution toward decreasing the importance of imported sulfur and helped in financing construction. Work on the plant began in 1952 and operation began in 1955. Capacity of the plant is 100,000 tons of acid and an equal amount of portland cement yearly and provisions are made for doubling this output if occasion offers.

Current employment of the two companies is about 1700 persons. In 1955 Albright and Wilson, Ltd., purchased the share capital of Marchon and Solway, an association providing a wider capital basis for any further expansion.

The anhydrite deposit at Solway is 100 feet below sea level (400 feet below

ground) and is 15 to 20 feet in thickness at area now being worked. Under St. Bees Head nearby, thickness is 80 feet and this is sufficient anhydrite for many decades of operation. Purity ranges between 88 and 95%. Chief impurities are calcium carbonate, magnesium carbonate, occasional inclusion of sandstone, and some iron oxide distributed as solid particles.

At the surface, the mined anhydrite undergoes primary and, when necessary, secondary crushing. The physical processing is shown diagrammatically in Figure 10. Final crushed product is all $\frac{3}{4}$ inch and is stored until needed.

Other raw materials required in the process are coke, to reduce the calcium sulfate, and shale, to give a portland cement clinker of desired composition. Material balance is shown in Figure 11.

Coke breeze from metallurgical and gas works, the only imported raw material, is brought to the plant by road or rail and conveyed to storage. The coke's

volatile content is an important factor. A low volatile content is desired as otherwise hydrocarbons from the coke are oxidized to water in the sulfuric acid plant converters; this water can help to cause emission of sulfuric acid mist from the stack, and can cause corrosion in the acid plant. Typical analysis of coke used at Solway (dry basis) is:

	%
Fixed carbon	80
Ash	14-18
Volatile materials	Less than 3

As received, coke normally contains 8 to 15% water.

Shale is quarried from a hillside adjacent to the plant. It is crushed and conveyed to raw material storage. Average analysis (dry basis) is:

	%
SiO ₂	60
Al ₂ O ₃	18
Fe ₂ O ₃	6
CaO	4
Alkalies	2-7

Shale as quarried usually contains about 12% water.

The raw material storage is adjacent to the drying building. Here wet material is conveyed to hoppers which feed standard double-pass rotary oil-fired dryers. Water content of coke and shale is reduced to 1 to 2%. Dryers are 5 feet 10 inches in diameter and 35 feet long. Coke and shale are normally dried in alternate runs in one dryer. There is another dryer for anhydrite which can alternatively be used for coke. Usually the water content of the anhydrite is sufficiently low that drying is not necessary.

Discharge of dryers is conveyed by skip hoists to separate raw material silos. These are made of heavily reinforced concrete and provide storage for 600 tons of anhydrite, 500 tons of shale, and 200 tons of coke.

The silos feed a sandwich of the three raw materials onto a belt by continuous electromagnetic belt weighers. These are adjusted to give:

	Parts	%
Anhydrite	150	78-80
Shale	30	14-15
Coke	12	6-7

or, based on analysis of cement clinker:

	%
CaO	65
SiO ₂	20
Al ₂ O ₃	7
Fe ₂ O ₃	3.2

The properly proportioned mixture is fed by rotary feed tables to two raw material mills. These are four-compartment combination tube mills, 7 feet 6 inches diameter and 40 feet long, operated by 850-hp. motors, and turn at 22 r.p.m. Discharge, called "raw meal," is 97% through a 170 mesh.

ized with compressed air, and pumped to concrete raw meal and blending silos. There are nine of these arranged in a square block and interconnected for blending.

In these silos, the mixture is blended by transferring between silos to give the final properly proportioned kiln feed. Finally meal is pumped by air to three silos which store corrected raw meal and which feed to hoppers and weigh feeders.

Approximately 10% water is added to the corrected meal in an open-plate nodulizer as a dust prevention measure and to lower kiln temperature. The nodules, $\frac{1}{4}$ to $\frac{1}{2}$ inch in size, are then fed to the kilns by gravity at controlled rates through special rotary pattern feeders.

Proper kiln conditions and operation are extremely important in the anhydrite process. All ratios of components are very critical and correct raw meal adjustment, and burning and atmospheric conditions in the kiln, are carefully controlled.

The two kilns are conventional cement kilns 11 feet 2 inches in outside diameter and 230 feet long. Each is supported by four sets of trunnions, and is operated by 120-hp. motors through fluid-drive coupling which permit regulation from 20 to 75 revolutions per hour. The normal speed is about 60 revolutions per hour. They are normally fired with washed, dried, pulverized coal, the moisture content of which has been reduced from 12 to -1% , and, have Diesel stand-by. Lined with 7- to 9-inch refractory and magnesite in hot zone, the kilns are designed to stand a maximum temperature of 1600°C . at firing end, this temperature being 200° higher than conventional cement practice. Actual operating temperatures are rather below 1600°C . Back-end temperature is between 350° and 420°C . Consumption of coal is about $\frac{1}{4}$ ton (wet) per ton of clinker. Feed enters at the cooler, elevated end and gravitates to the hot firing end.

In the kiln, the three reactions take place:

1. Reduction of anhydrite by coke



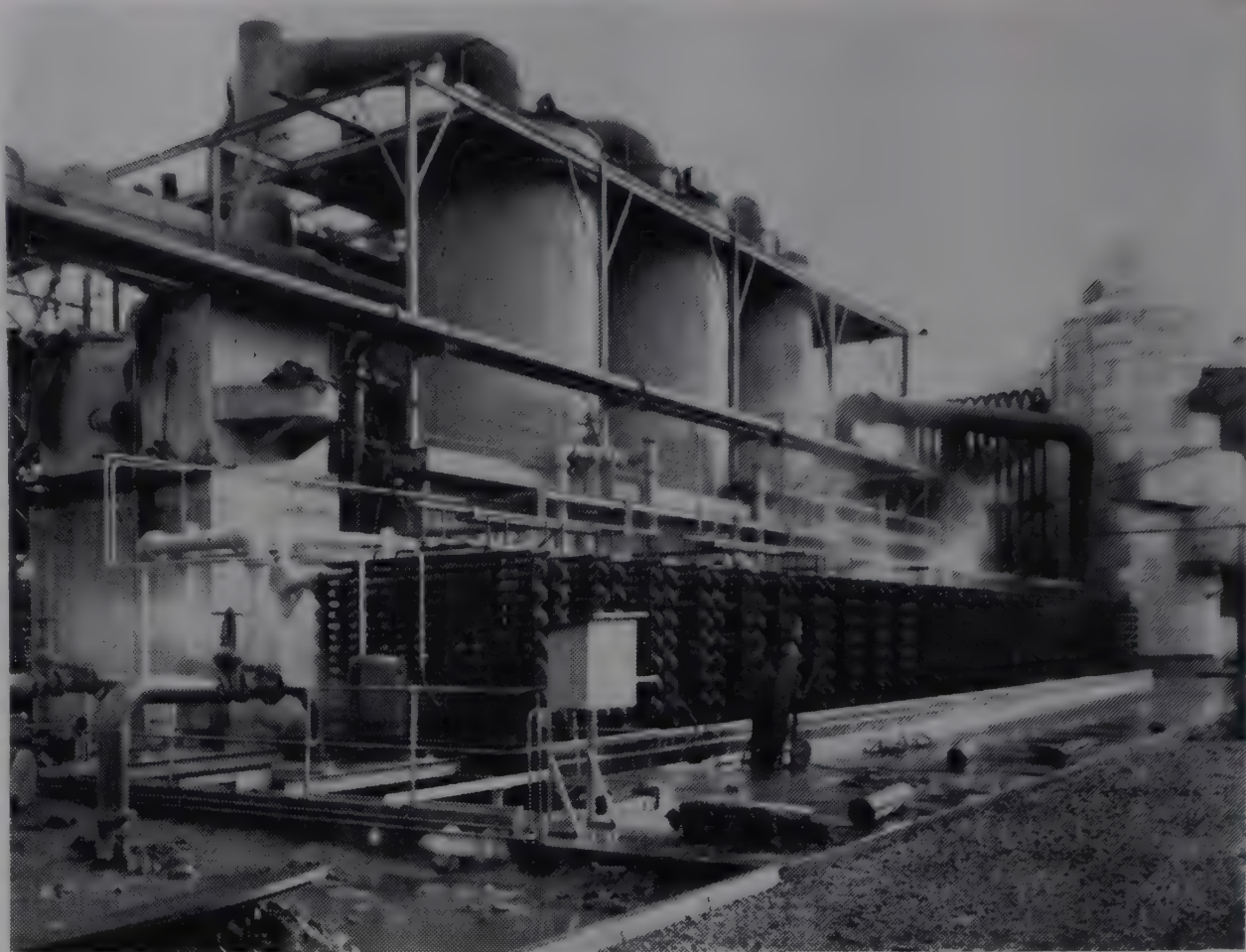
2. Reaction of calcium sulfate and calcium sulfide freeing sulfur dioxide gas and forming lime



3. Direct reaction of calcium sulfate and acidic oxides to give clinker compounds.

Clinker is discharged at rate of 135 to 150 tons per day per kiln

Calcium sulfide and calcium sulfate must be kept within limits to prevent erosion and deterioration of lining. An



In the absorbers, sulfur trioxide is absorbed in sulfuric acid. Water is added to keep concentration constant. Either 98.5% acid or oleum can be made

important ratio is that of carbon to sulfur trioxide. The gas leaving the cold end contains about 9% sulfur dioxide.

Clinker from the kiln passes through rotary coolers which also heat kiln combustion air. It is then passed through automatic weighers to storage. From storage, it is weighed again and conveyed to the cement plant where 3 to 5% gypsum is added to retard setting time of finished product. This mixture goes to conventional combination tube mills and final product to cement silos for eventual packing in 112-pound paper bags or bulk loading.

The cement, which fully meets British specifications, is marketed by The Associated Portland Cement Manufacturers Ltd. Most of it is used within an 80-mile radius, a good part to date being used by the U. K. Atomic Energy Authority which is erecting atomic power plants in this area.

Solway Plant Uses Contact Process

With exception of more extensive gas cleaning and cooling sections, the Solway acid plant is fairly conventional in design and operation.

The wet dirty gases from the two kilns are kept in two streams for processing in two parallel, similar plants. They first pass through cyclones by way of cooling mains and then to a 50,000-volt electrostatic precipitator where 50 to 60% and 50 to 40% of dust are removed, respectively. The over-all efficiency of dry dust removal is over 99.5%. The last trace of dust is removed in a wash tower further in the processing

line. Fine dust, containing undesired alkalis, is discarded; balance of recovered dust is returned to raw meal silos. The cleaned gas is drawn first upward through an empty wash tower, which is lead- and brick-lined, and through which water flows downward through the hot gases which are cooled to about 50°C . Exit gases pass through coiled lead gas coolers where temperature is reduced to about 30°C . The run-off water (made slightly acidic by contact with the gases) is recycled after cooling in lead-coil coolers. The two gas streams, now saturated with water, pass through lead mains to three parallel pairs of electrostatic precipitators, where mist and last particles of dust are removed.

The clean, moist gas is diluted with air and passes upward through two ceramic ring packed drying towers in which 98% sulfuric acid flows downward to remove final moisture. From the drying towers the gas is sufficiently dry for mild steel to be used for conveying pipes and plant equipment. Final gas, now perfectly dry, contains about 5% sulfur dioxide. Dried gas is drawn by plant blowers operated by 450-hp. motors. These provide suction from hot end of kiln and force gases under slight pressure to converters and waste gases to tail gas filters and stack.

The converters and heat exchange systems are conventional. The lagged 5-stage, 4-pass converters are constructed of mild steel and are brick-lined and contain vanadium pentoxide catalyst in extruded granule form. From the converters, the hot sulfur trioxide gas at 420°C ., is cooled to 160°C . in external



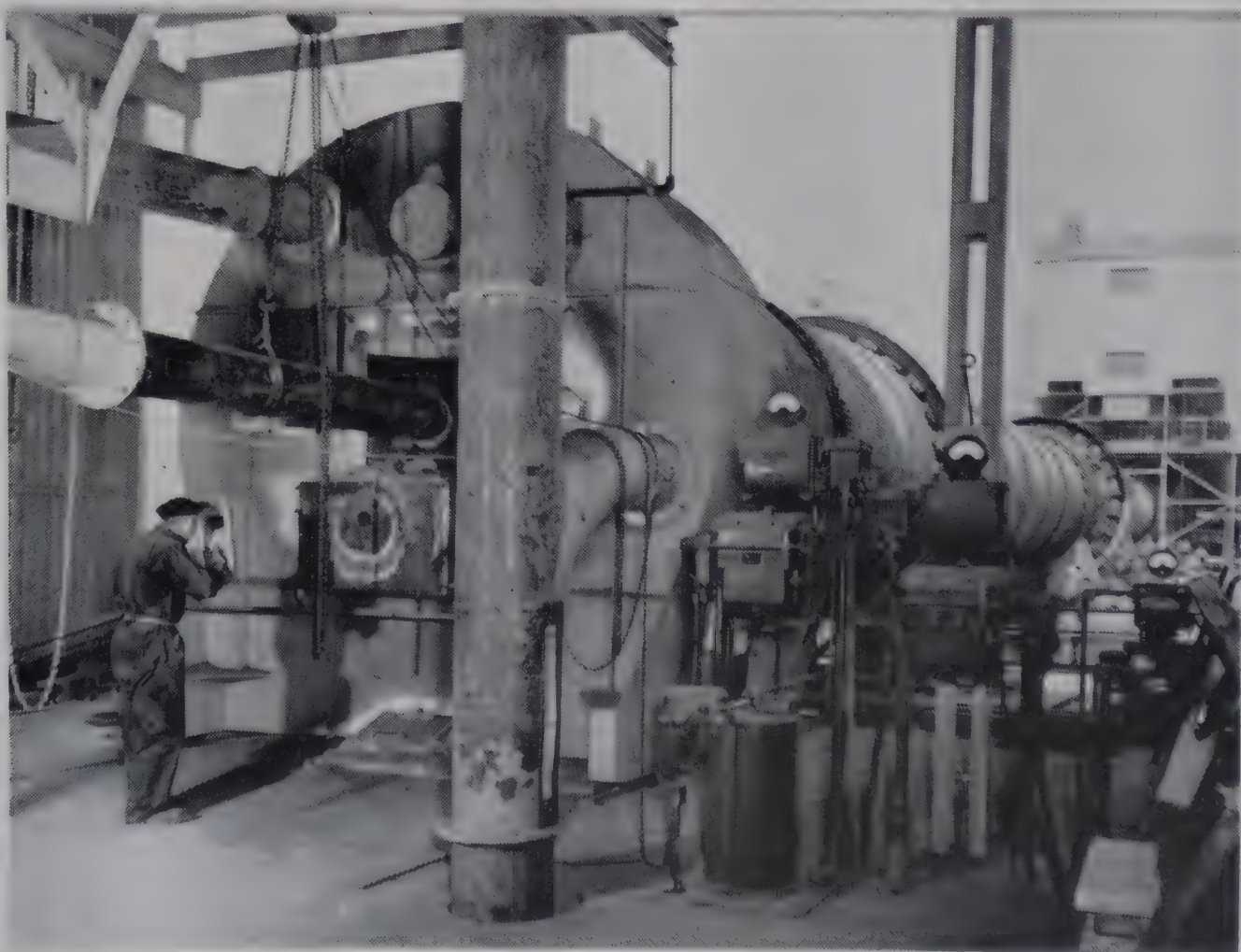
Shale is quarried from a hill near the plant. Coke arrives by rail. Both go to the raw materials storage



Rotary kilns, dominating feature of all cement plants, are 230 feet long. Right, rotary clinker coolers



Properly proportioned mixture of anhydrite, shale, and coke is ground in tube mills and then pumped to raw meal silos



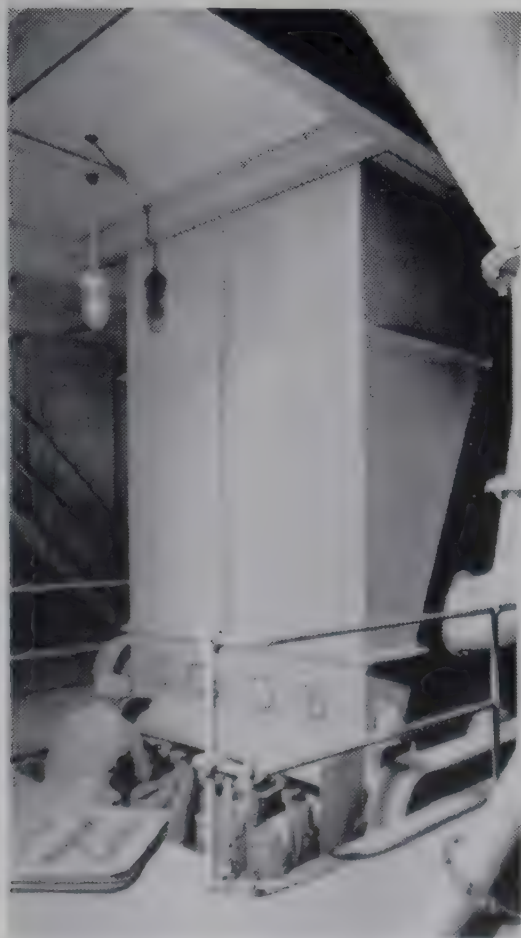
Kiln temperatures in the anhydrite process are higher than in normal portland cement operation. Kiln conditions must be closely regulated



Contact sulfuric acid plant is fairly conventional in operation. Left to right. Converters, absorbers, and acid coolers



Extensive cleaning and cooling of kiln gases are accomplished in the wash tower, lead coil coolers, and electrostatic precipitators



Ground cement is either bagged or bulk loaded



heat exchangers, and then passes to the absorbers. These are ceramic-packed towers in which both 98.5% acid and oleum are produced. Final products, respectively, go to a tank farm consisting of nine 1000-ton and two 500-ton mild steel storage tanks, jointly used by Marchon and Solway.

A feature of the anhydrite process is that the tail gases after absorption are more misty than the tail gases from sulfuric acid plants using sulfur or pyrites as raw materials. This has been found to be connected with the synthesis of oxides of nitrogen in the flame of the kiln.

In this plant, the mist is eliminated by drawing the misty gases through porous beds at high velocity. This

	Anhydrite	Sulfur	Pyrites
Raw materials	6.16	14.56	13.16
Conversion, including fuel	11.48	2.80	6.16
Overhead, interest and depreciation	10.92	3.36	7.00
Total	28.56	20.72	26.32
Less credits	5.88	0.84	0.84
Net cost	22.68	19.88	25.48
Capital cost	95.20	26.60	54.60

agglomerates the mist particles to coarse droplets which are recovered in a simple drop-catcher.

Two blowers of 300 hp. each are used for drawing the gases through the porous material.

The acid recovered in the mist filters is high in nitrogen content. It is segregated and mixed with sulfuric acid supplied to the nearby phosphoric acid plant, where nitrogen content is not critical. The rest of the sulfuric acid is of standard quality, and is used for surface active agents and for general sale.

A pipe line runs from the storage tanks to the Marchon plant a short distance away. At Marchon, phosphate rock brought from French North Africa is digested with sulfuric acid to form 40% phosphoric acid, principally used as raw material for alkali phosphates.

Marchon consumes most of Solway's acid output. Balance is sold on the open market.

Capital Requirements and Production Costs

A plant for the production of 75,000 to 150,000 tons of sulfuric acid from anhydrite has been estimated to be between \$84.00 and \$106.00 per ton year of sulfuric acid at mid-1953 prices. These figures include surface site development and working capital but not capital costs of mine and plant to produce cement from clinker.

Ratio of capital cost of anhydrite sulfuric acid and that of acid from pyrites is about 1.5 to 1. In the U. K. minimum economic capacity for an anhydrite

Principal Uses of Sulfuric Acid in U. K.

Year	Phosphate Fertilizers	Sulfate of Ammonia	Rayon	Dyes	Paints and Pigments	All Other Uses	Total
1949	1280	720	430	200	300	1670	4600
1950	1190	730	550	240	370	1900	4980
1951	970	730	520	240	360	1760	4580
1952	1010	760	320	120	290	1740	4240
1953	1320	790	540	190	500	1870	5210
1954	1250	800	580	230	620	2130	5610
1955	1340	780	595	215	680	2195	5805

acid plant has been estimated to be 50,000 tons of acid per year.

Production costs of contact sulfuric acid in the U. K. (mid-1953) have been estimated for plants of 60 to 70,000 tons annually (in dollars):

Approximate Labor Costs

	% of Labor	
	Force	Cost
Mine (total underground and surface)	36.5	36.5
Raw materials preparation, including shale quarrying and preparation	8.5	8.5
Kiln operation and dust recovery	7.5	8.5
Gas cleaning and acid plant	4.0	4.7
Cement production, packing and dispatch	4.5	3.5
General labor	4.0	3.5
Maintenance	22.5	22.2
Laboratory control	10.3	8.5
Supervision and overhead	2.0	4.1

Materials Balance

Required for 1 Ton of H_2SO_4 (100%)

	Tons
Anhydrite (based on 94% purity)	1.65-1.80
Shale (as quarried)	0.35-0.36
Coke (as received)	0.14-0.15
Clinker	1.04
Nodulizing water	0.22
SO_2	0.674
SO_3	0.82

Services

Coal, tons	0.25
Total water, gal.	3600
Electricity, kw.-hr.	280-300
(including mining, cement production, and packing.)	
Oil (drying), lb.	32

Cost data are taken from lecture presented by Bedwell in 1952 and updated (7). All conversions on basis of \$2.80 per pound sterling.

At that time, cost of sulfuric acid from anhydrite was lower than that from pyrites, although capital cost was higher. Emphasis is made that the costs are only indicative as both capital and production costs vary with output, plant location, and other factors.

Marchon's most recent costs estimates show an improvement on these figures.

Future of Process

In the U. K., the sulfur picture has changed markedly since the Solway anhydrite plant was planned. New discoveries of sulfur in the U. S. and elsewhere, ending restrictions on export of sulfur to Great Britain, have resulted in a decrease in interest in the anhydrite process.

However, production of sulfuric by the process is claimed to be as cheap as from any postwar plants in the U. K. using any raw material. Cement is sold at market value. Too, any operation which cuts back on imports is looked upon very favorably. Solway has experienced no great difficulty in marketing its surplus acid in a very competitive situation and provision has been made for further expansion.

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Potassium Borohydride Manufacture

WALTER S. FEDOR

Associate Editor in collaboration with

M. DOUGLAS BANUS and DAVID P. INGALLS

Metal Hydrides Inc., Beverly, Mass.

EXOTIC FUELS have captured the public's fancy these past few months. These high energy "zip" fuels—used to power rockets and guided missiles—are regarded by many as an important key to our nation's defense. Often included as "zip" intermediates are metal hydrides such as sodium borohydride, calcium borohydride, and lithium borohydride.

But often overlooked by the trade and popular press are the growing commercial (nonmilitary) uses for these compounds. Sodium borohydride, for example, is a known reducing agent. And so is sodium borohydride's cousin, potassium borohydride. But unlike its relative, the latter compound has no military potential. A low volume item now, its future market will depend upon commercial "break-throughs" such as has happened when potassium borohydrides reducing properties were put to use in pharmaceutical synthesis.

Metal Hydrides Inc., Beverly, Mass. is the only commercial potassium borohydride producer in the United States. The material is made in limited amounts in Europe by Rhône-Poulenc, a French firm (8). A licensing agreement allows

Metal Hydrides to market in Europe now.

The company was founded in 1937 to manufacture metals or metal alloys by the use of hydrides (or other processes), which used ores, oxides, or other compounds of the metals concerned such as titanium, calcium, zirconium, and tantalum. Later the company added alloy powders to its product line. In 1948 the firm started to make double hydrides such as lithium aluminium hydride, sodium and potassium borohydride—the latter in 1952.

This year the company hopes to sell around 20,000 pounds of potassium borohydride—almost a 1000-fold increase over 1952's meager 22 pounds. By 1960 it is possible that potassium borohydride's output will near 100,000 pounds. Beyond that date it is difficult to predict; potassium borohydride is very much in demand as an experimental product.

Growth since 1952 has been mostly in the pharmaceutical industry. Here it has been used as a reducing agent to make hydrocortisone, prednisone, and prednisolone, well-known corticosteroids used in arthritis therapy. In addition,

Process Economics

Potassium borohydride can be made continuously, and economically, if it is produced at a rate between 2500 and 3000 pounds per day. Here is an estimate of what a 2800-pound-per-day continuous plant would cost:

Plant investment

Equipment costs	\$ 480,000
Piping, instrumentation facilities	420,000
Site preparation	60,000
Buildings	180,000
Engineering and other costs	540,000
Total	\$1,680,000

Per Pound of Product

Operating costs

Raw materials (including credits)	\$1.90
Labor	0.20
Maintenance	0.07
Utilities	0.07
Factory overhead	0.20
Tank car and trailer rentals	0.12
Depreciation, taxes, etc.	0.43
Total	\$2.99

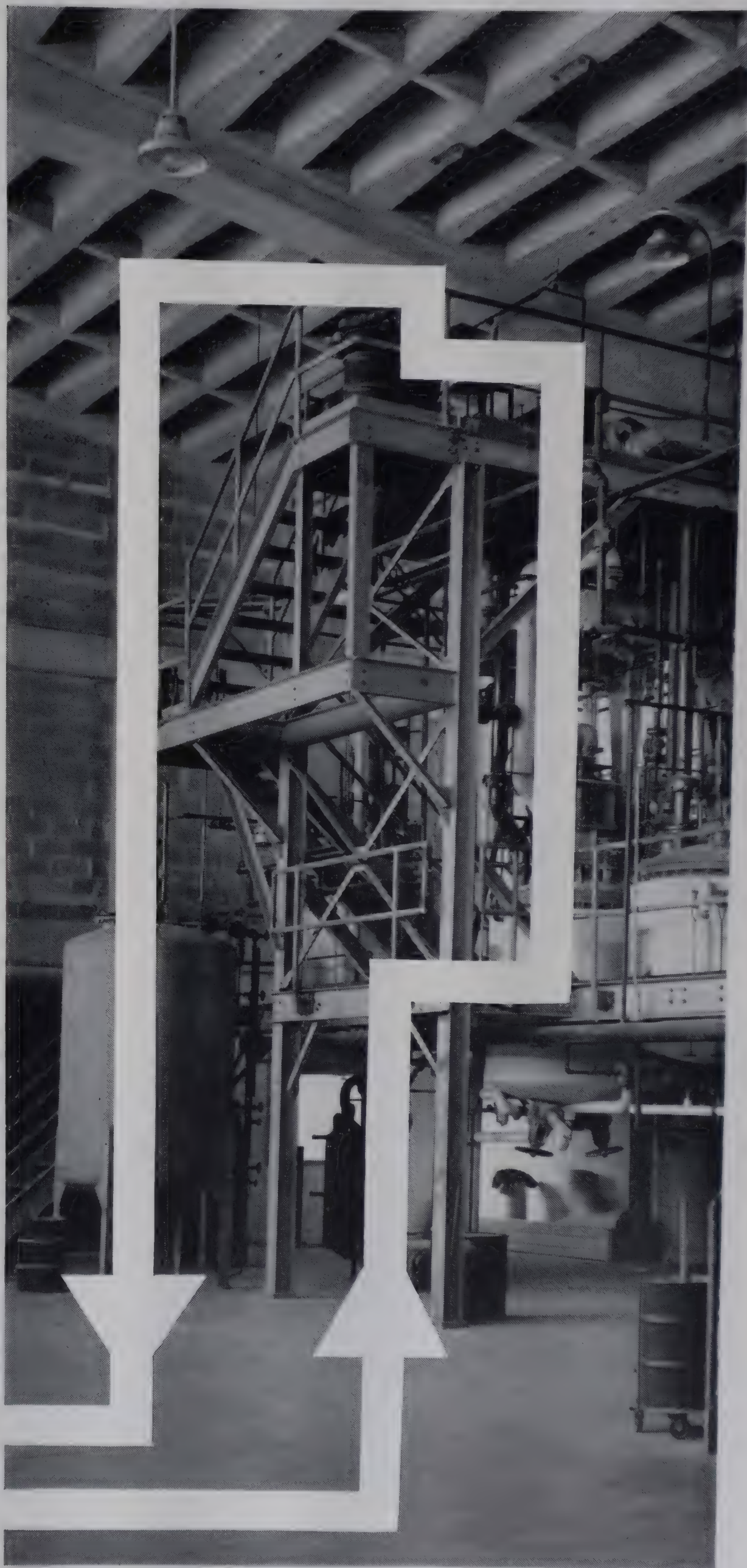
potassium borohydride is used in Vitamin A synthesis. These uses consume 80 to 90% of the potassium borohydride made.

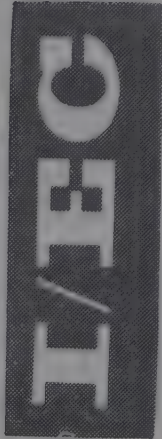
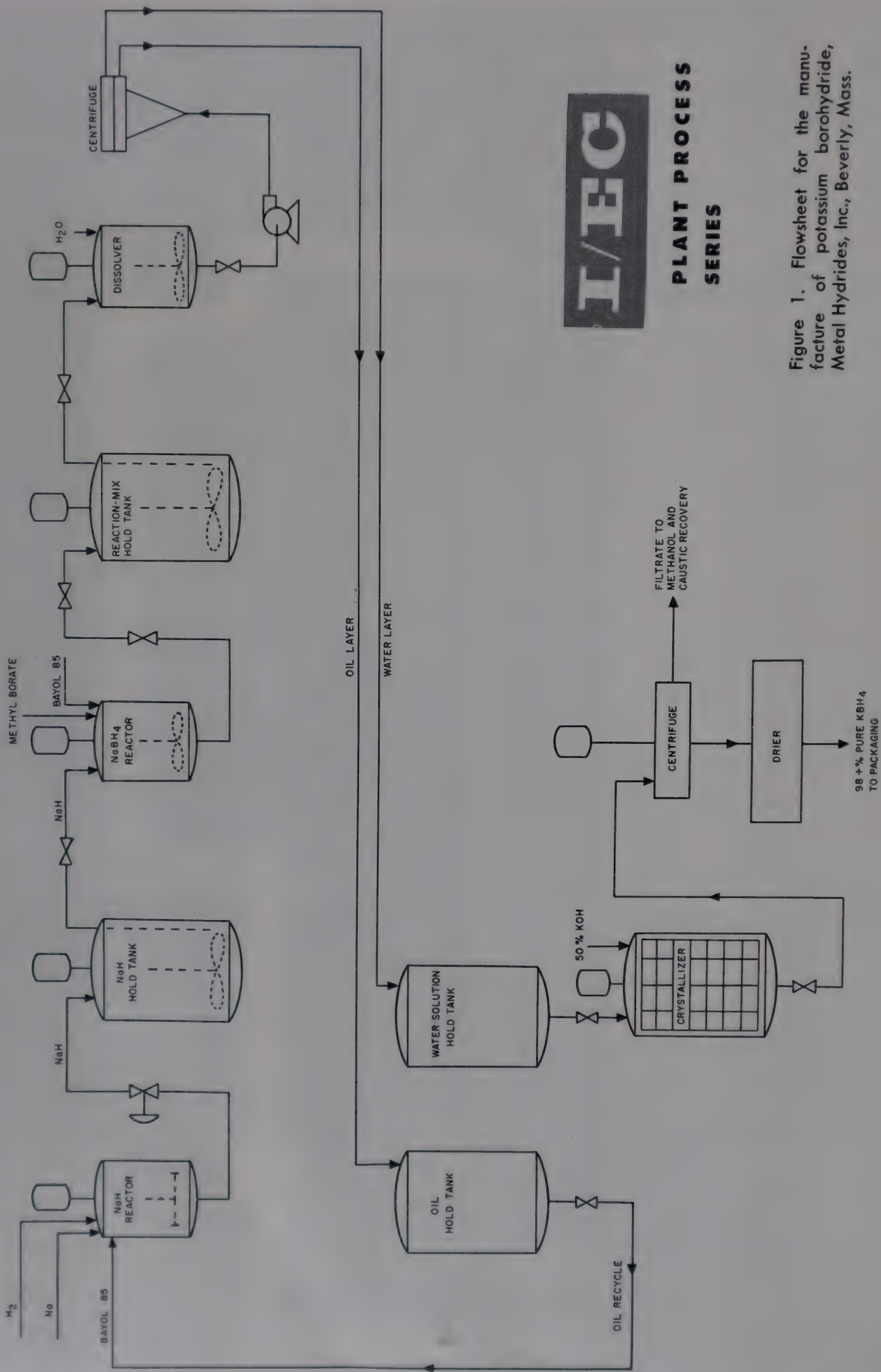
The remaining 10 to 20% made today goes for experimental uses. Results known give hope that potassium borohydride demand will grow in areas such as foam plastics or similar materials; cellulose modification; and bleaching agent for pulps. There are other possibilities, too, many capable of turning potassium borohydride into a large volume product.

Like Sodium Borohydride

Potassium borohydride is similar to sodium borohydride in that it easily reduces the carbonyl group of aldehydes, ketones, and acid halides. During the reduction process other functional groups are not affected, nor are olefinic double bonds attacked. Cases have been reported (5) where solutions of potassium borohydride and lithium chloride, in tetrahydrofuran, allow ester reduction with fair yields.

Potassium borohydride is unique among the hydrides in being completely stable in air, under normal atmospheric



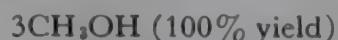


PLANT PROCESS SERIES

Figure 1. Flowsheet for the manufacture of potassium borohydride, Metal Hydrides, Inc., Beverly, Mass.

conditions. This property also simplifies its manufacture. Conventional processing equipment can be used with routine safety measures.

Metal Hydrides makes potassium borohydride under its basic process patent (7). In it, potassium borohydride is made by precipitating an aqueous-alcoholic solution of sodium borohydride with sodium and potassium hydroxides. The entire process can be stated as follows:



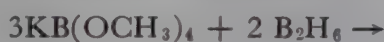
This method is really a long way to the end product. The most direct route to alkali metal borohydrides is a straight forward reaction between the alkali metal hydride and an alkyl borate (3). This works well for sodium borohydride but it is a costly method to potassium as well as cesium and rubidium borohydrides. A major reason is the reaction—75% of the alkali metal used ends up as the alkoxide or as the hydroxide as shown in the equations. In addition, potassium's reactivity is low hence it requires excess hydride. With potassium selling for \$3.66 per pound, the cost becomes prohibitive (4).

Another route to potassium borohydride involves making potassium tetramethoxyborohydride from potassium and methyl borate (7). The tetra compound is then reacted with diborane to make potassium borohydride. The re-

Potassium Borohydride's Properties

Formula	KBH_4
Molecular weight	53.95
Purity	98% +
Form and color	White crystalline solid.
Melting point	Decomposes in vacuum without melting at about 500° C. Hydrogen evolved. Above 500° C., potassium distills.
Density	1.175 grams per cc.
Heat of formation	-57.5 kcal. per mole
Heat of hydrolysis	-62.65 kcal. per mole
Reduction potential	Standard EMF, + 1.23
Refractive index	1.494 at 20° C.
Thermal stability	Stable to 500° C. in vacuum. Ignites from free flame in air. Burns quickly. Will not ignite at 300° C. on a hot plate.
Storage and handling	Can be handled in air safely and stored at ordinary conditions, says Metal Hydrides. It is nonhygroscopic under normal atmospheric conditions. Stable in air.
Stability in water	Reacts insignificantly in cold water.

action goes as follows:



The method never advanced beyond the laboratory stage.

Metal Hydride's Process

Potassium borohydride manufacture, as used by Metal Hydrides, is a semi-continuous process. Production runs between 80 and 100 pounds a day when "on stream." The plant is now in use 200 to 250 days a year, depending upon demand. Process equipment used by

Metal Hydrides is flexible. Many units are commercially available items readily obtained from equipment manufacturers. When not used to make potassium borohydride, the company can use some of its equipment to make other products such as sodium hydride and sodium borohydride. This means Metal Hydrides uses an integrated facility, a practice of many companies which produce low volume items.

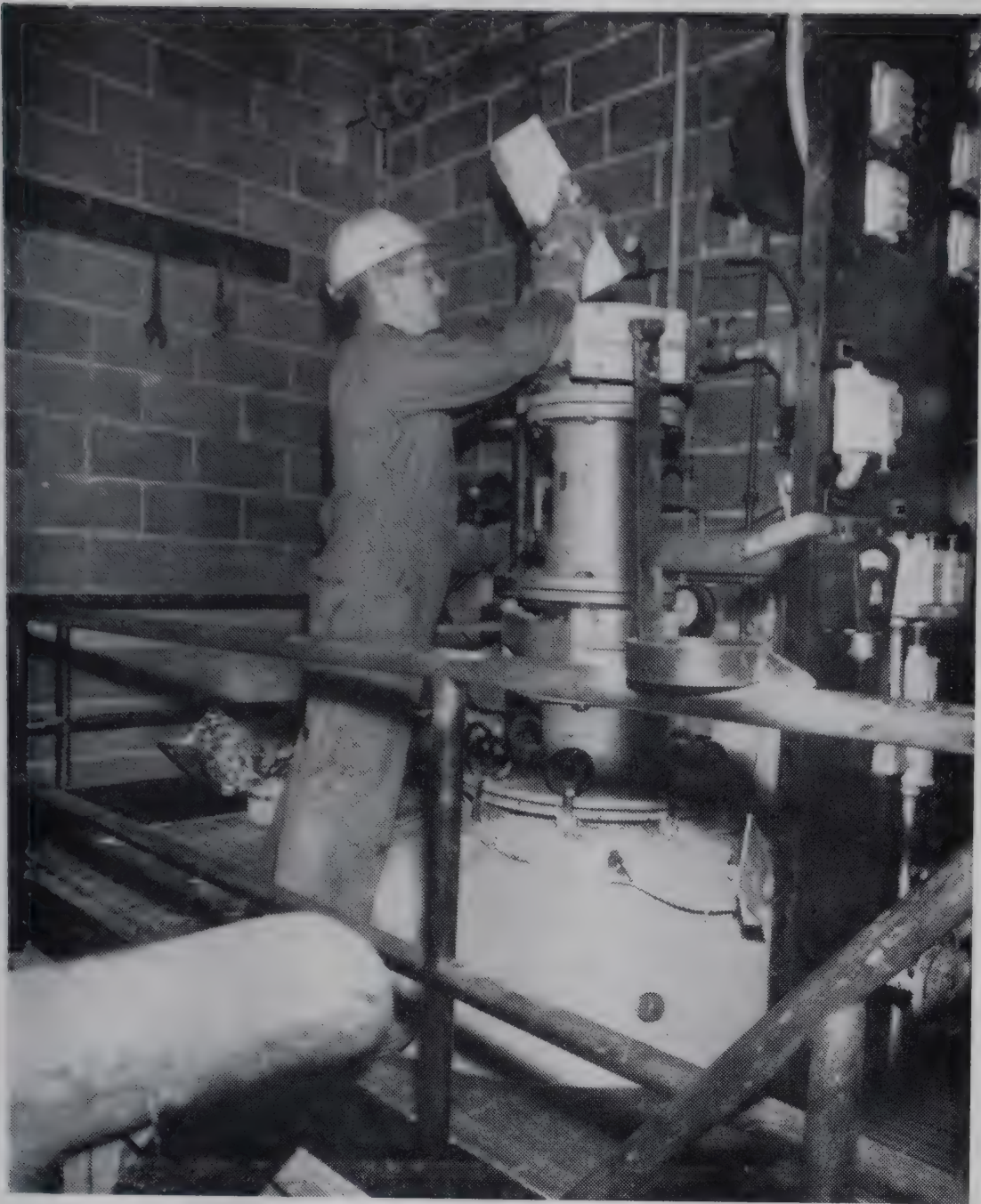
When units are changed over from one process to another the reactors are washed out with water and detergent. Then the vessel is washed with a solvent such as methanol or water which will be used in the next process. The reactors are then dried with heat and vacuum (most vessels are steam jacketed).

Briefly, Here's How to Make Potassium Borohydride

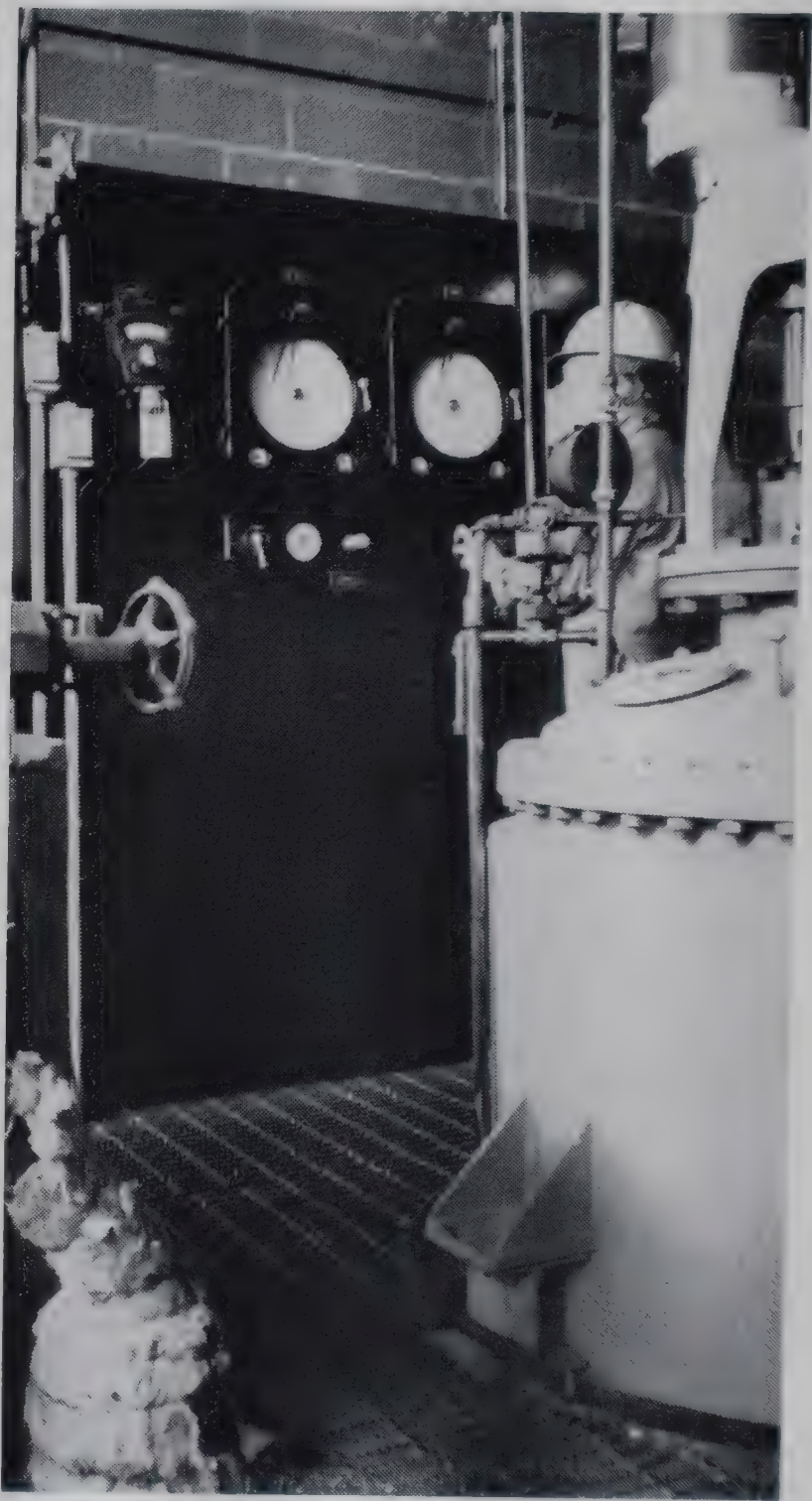
- ▶ Melt sodium, vigorously agitate in oil with hydrogen—to form sodium hydride dispersion
- ▶ Add methyl borate to make sodium borohydride and sodium methoxide
- ▶ Dissolve mixture in water and make two-phase system; separate oil layer
- ▶ Treat water layer with potassium hydroxide to precipitate potassium borohydride
- ▶ Separate potassium borohydride, dry, package for shipment



Hydrogen used in the process arrives in tube trailer trucks—a total of 48,000 cubic feet per truck. Trailers are left at a hydrogen-unloading system, then tanks are connected and the hydrogen is fused directly from the tanks as needed



◀ Potassium borohydride's manufacture starts by dropping sodium bricks into the melt tank



Sodium hydride-methyl borate reaction to make sodium borohydride calls for careful watching of the pneumatic controls. They are important and must be kept between 250° and 270° C.



◀ Temperatures, hydrogen flow, and sodium weight must be checked continuously in making the sodium hydride dispersion

If potassium borohydride's demand increases and a separate plant should be built to make it, there would be little technological change other than to make it completely continuous. This would not be economical unless potassium borohydride were made at a rate of 2500 to 3000 pounds per day.

Sodium, hydrogen, a mineral oil, and methyl borate are the major raw materials used to make potassium borohydride. Metal Hydrides buys its sodium from Du Pont and U. S. Industrial Chemicals, Division of National Distillers and Chemicals, at prevailing market prices. (Usually about \$0.17 per pound.) It is shipped to Beverly by truck in 280-pound net barrels of 12.5-pound bricks, 23 bricks per barrel, and stored in the warehouse until needed.

Hydrogen, bought from New England Gas Products, is shipped by tube trailer truck. Each trailer has 38 tubes for a total of 48,000 cubic feet. The trailers are backed up to a hydrogen unloading system, tanks are connected and hydrogen is used directly from the tanks as needed.

The mineral oil used in the process (Bayol 85) comes from Esso Standard Oil. It is stored in the immediate process area. Oil used in the process is usually recovered completely, hence make-up volume is small. Methyl borate is made at the Beverly plant and piped to a 200-gallon storage tank in the processing area for use as needed.

First Make Sodium Hydride Dispersion

Metal Hydrides starts to make potassium borohydride by dispersing sodium hydride in inert mineral oil (Figure 1). Sodium bricks are dropped by hand into a 1000-pound-capacity heated melt tank. Under a nitrogen atmosphere sodium is melted at 100° C. (just above its melting point 97.5° C.).

Melted sodium is then "pushed" by nitrogen into a 200-pound-capacity weighing tank insulated with magnesia bricks. The unit is attached to a Toledo dial scale which operates semiautomatically. When a charge enters the weighing tank, the scale is engaged. When the peak weight is reached, it is released, the melted sodium being pumped continuously into a sodium hydride reactor. Normal flow rate is around 250 pounds per hour.

The sodium hydride reactor was designed by Metal Hydrides; it has characteristics which are the subject of a patent application and cannot be released at this time. In it a finely divided sodium hydride in oil dispersion is made—a key process step.

Sodium metal is agitated with Bayol 85 and hydrogen to make the disper-

sion. A turbine agitator which rotates up to 8000 r.p.m., breaks the sodium into very small particles. Dispersal or hydriding accelerating agents are not needed (7).

Reaction temperatures start at about 200° C. and rise as high as 350° C. The reaction peak is usually reached somewhere between 260° and 290° C.

Hydrogen at atmospheric pressure or a bit higher is continuously metered to the reactor through a pressure controller (a rotameter can be used for visual flow observations). About 359 cubic feet of hydrogen are needed for every 46 pounds of sodium. The final dispersion contains 25% sodium hydride and 75% oil. Yield is 98%.

The sodium hydride-oil dispersion is withdrawn continuously at about 1000 pounds per hour (250 pounds of sodium hydride) through a liquid level controller unit into one of three 1000-gallon storage tanks. Here the product is cooled to about 250° C. and is kept dispersed by an agitator which runs about 360 r.p.m. At this step, the dispersion can be pulled out for salable product.

Next Major Step—Make Sodium Borohydride

The sodium hydride-oil dispersion is then pumped from a storage tank into a reaction vessel—specially designed by Metal Hydrides—where sodium borohydride is made. Exact details cannot

A Look at Metal Hydrides Inc.

Metal Hydrides was incorporated on June 16, 1937. Its manufacturing plant, offices, and laboratories are located in Beverly, Mass., about 20 miles northeast of Boston. The firm also owns 80 acres of land at Danvers, not far from Beverly.

The company's start was an outgrowth of a doctoral thesis by Peter P. Alexander, now the firm's Chairman of the Board. He found that hydrogen released from a hydride had high reducing properties and that it could be used in certain metallurgical applications.

At first Alexander used tantalum hydride as a source of hydrogen. Later other cheap hydrides were found useful and it became evident that this method could be developed into a commercial process for the production, in a pure state, of such metals as titanium, zirconium, chromium, and uranium. Such was the beginning of the company.

Later on, chemical hydrides were added to the firm's product list. Today, calcium and sodium are the most important binary hydrides. Also, the company makes double hydrides with aluminum and boron. It still makes metal powders, and alloy powders from chromium, thorium, titanium, and zirconium. These materials usually go to the metallurgical and electronics industries.

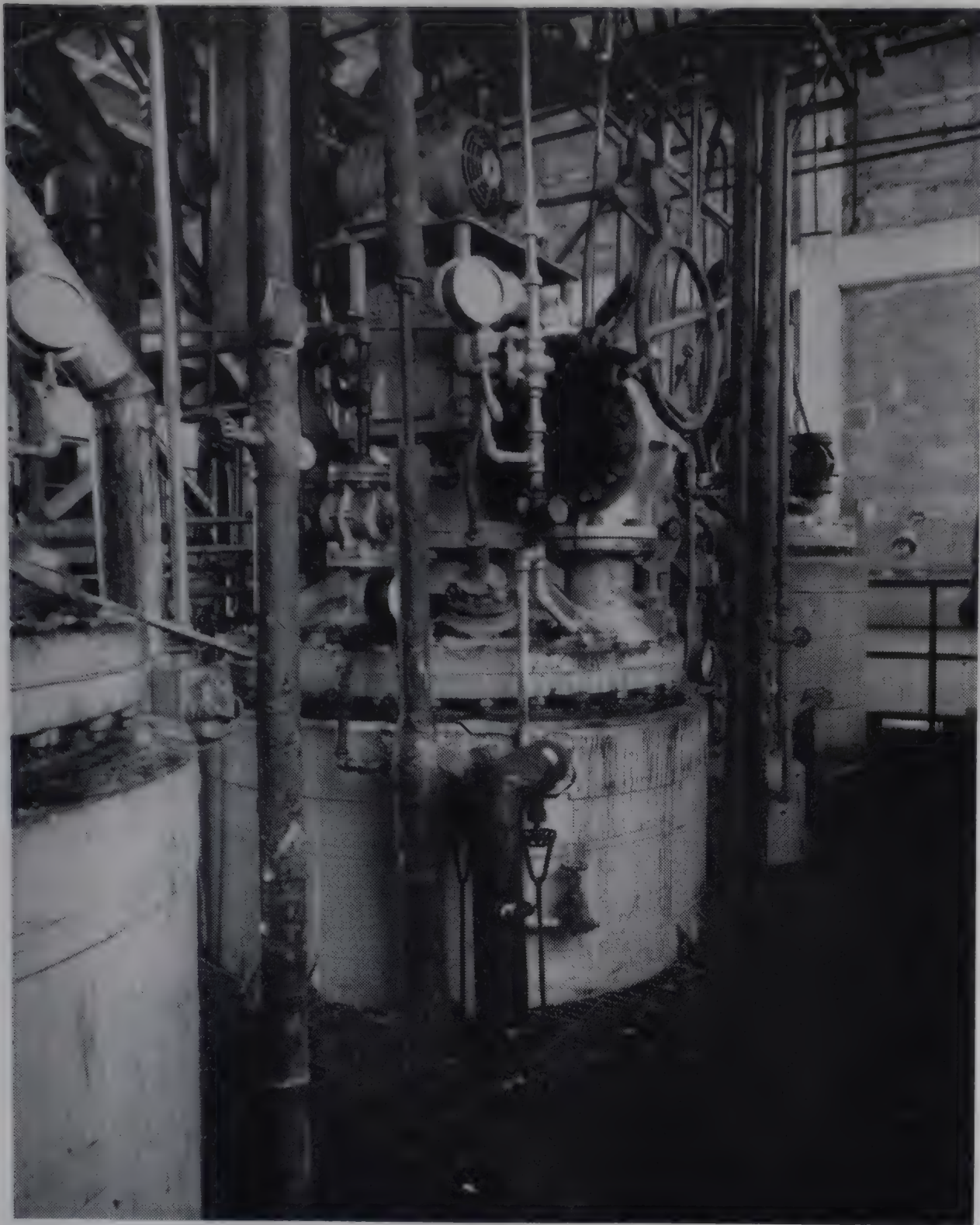
The company received a Navy contract in May 1956 in which Metal Hydrides has agreed (9) to design and install equipment to make sodium borohydride at an estimated cost of nearly \$4.4 million to the Government. Cost to Metal Hydrides will near \$1 million. The plant will take up about 10 acres at the Danvers site. Hence there is still room for 70 acres in expansions.

Last year commercial sales of the company's products reached nearly \$1.5 million (6). This was a decline over 1955 but it was due to completion of a government order. On the other hand, the company's chemical products have shown steady gains, reaching nearly \$1.2 million in 1956, compared to \$607,000 in 1955 and \$346,000 in 1953. Even greater growth in chemical product sales is expected in the future. Important too, to Metal Hydrides' thinking, the ratio of civilian sales to total sales, is rising. In 1956, about 62% of sales went to civilian markets; compared to 23% in 1955, and 21% in 1954.

Mineral Oil Dispersion

The mineral oil dispersion is the key step to potassium borohydride made at Metal Hydrides. Here's why:

- ▶ Sodium hydride is made faster than in any previously known method by hydriding a dispersion of sodium metal in oil.
- ▶ Sodium hydride-oil dispersions are easier to handle than dry powdered sodium hydride of equivalent reactivity.
- ▶ Dispersion reacts with methyl borate about 10 times faster than sodium hydride made any other way.
- ▶ Reaction with hydride dispersion and methyl borate is efficient and rapid with stoichiometric amounts; excess hydride not needed.
- ▶ Large volume of oil absorbs heats of solution and reaction from sodium methylate, excess sodium hydride, and sodium borohydride. Decomposition from overheating is avoided.



Sodium hydride and sodium borohydride are made by a continuous process. Then it becomes a batch operation. This starts when the sodium borohydride reaction mixture is dissolved in water, making as the end result a two-phase system—70% oil and 30% water. The vessel used is called the dissolver

be revealed but the vessel has a 150- to 200-gallon capacity. It is jacketed and magnesia brick insulated. Electrical heating elements heat oil, which in turn, control the heat during the reaction. Inserted in the reaction vessel is an agitator.

The borohydride reactor is heated to between 250° and 270° C. Hydride dispersion from a storage tank and methyl borate from its storage tank in the process area, are simultaneously pumped to the reactor and mixed in a 4 to 1 ratio. The mixture is stirred for about 1 hour.

The resulting product is a reaction mixture in oil which has from 3 to 8% sodium borohydride and 12 to 30% sodium methoxide. There are also trace amounts of sodium hydride. This step usually gives a 95% yield.

If sodium borohydride is needed for sale it can be separated from the above

mixture by a solvent such as liquid ammonia or ethylenediamine. These solvents are selective for sodium borohydride but not sodium methoxide or the mineral oil.

For potassium borohydride manufacture, the mixture is pumped, at a rate near 200 gallons per hour, to a water-jacketed cooling tank. City water at line temperature is used as the coolant. After cooling to around 200° C. it is pumped to a 1000-gallon hold tank.

Splitting Comes Next

The potassium borohydride process now becomes a batch operation because most of the equipment is used to make other chemicals. The sodium borohydride mixture is transferred from the hold tank to a dissolver, a 300-gallon stainless steel tank. About 2000 pounds of the borohydride mixture is pumped

Load Cells Solve a Crucial Problem

Amount of reactants needed in the step to make sodium borohydride is crucial. Metal Hydrides solved this problem via a load cell weighing system which uses strain gage load cells as fixed, integral parts of the reaction vessel (2). Three brackets, welded to the tank bottom are the supports. Each bracket rests on a 2000-pound-capacity load cell, which is water cooled to prevent the heat from the tank reaching the cell.

Cell impulses are transmitted to an instrument panel. Usually, only the initial-charge weight is recorded but the system allows reading at any reaction stage. Weights are shown as an indicator mounted on a nearby instrument panel. Tank weight is tared from the indicator. Weight accuracy is $\pm 0.25\%$ of original charge.

Cells used are made by Baldwin-Lima-Hamilton and are temperature compensated—hence, no moving parts. These cells are not affected by moisture or gases.

into the unit. Between 600 and 700 pounds of demineralized water is added and the mass agitated at 100 to 200 r.p.m. from 1 to 3 hours.

Enough water is added to dissolve all the sodium borohydride as well as the caustic soda formed by reaction of excess sodium hydride with the water. More caustic comes from the reaction of sodium methylate with water. And methanol is a by-product of the methylate-water reaction. There is a rise in temperature here so the dissolver is water-jacketed and cooled with city water. Product temperatures do not rise above 30° C.

When the reaction is complete the entire mixture is pumped to a hold tank adjacent to the dissolver. At this point the process liquor is a two-phase system—roughly 70% oil and 30% product liquor.

This dual system is then pumped to a continuous liquid separator or centrifugal splitter where the oil is split from the aqueous layer. The splitter can handle about 300 gallons an hour.

The separated oil is cycled to a hold tank and, after assay, is pumped back to the oil storage tank for re-use in the

Solubility of Potassium Borohydride

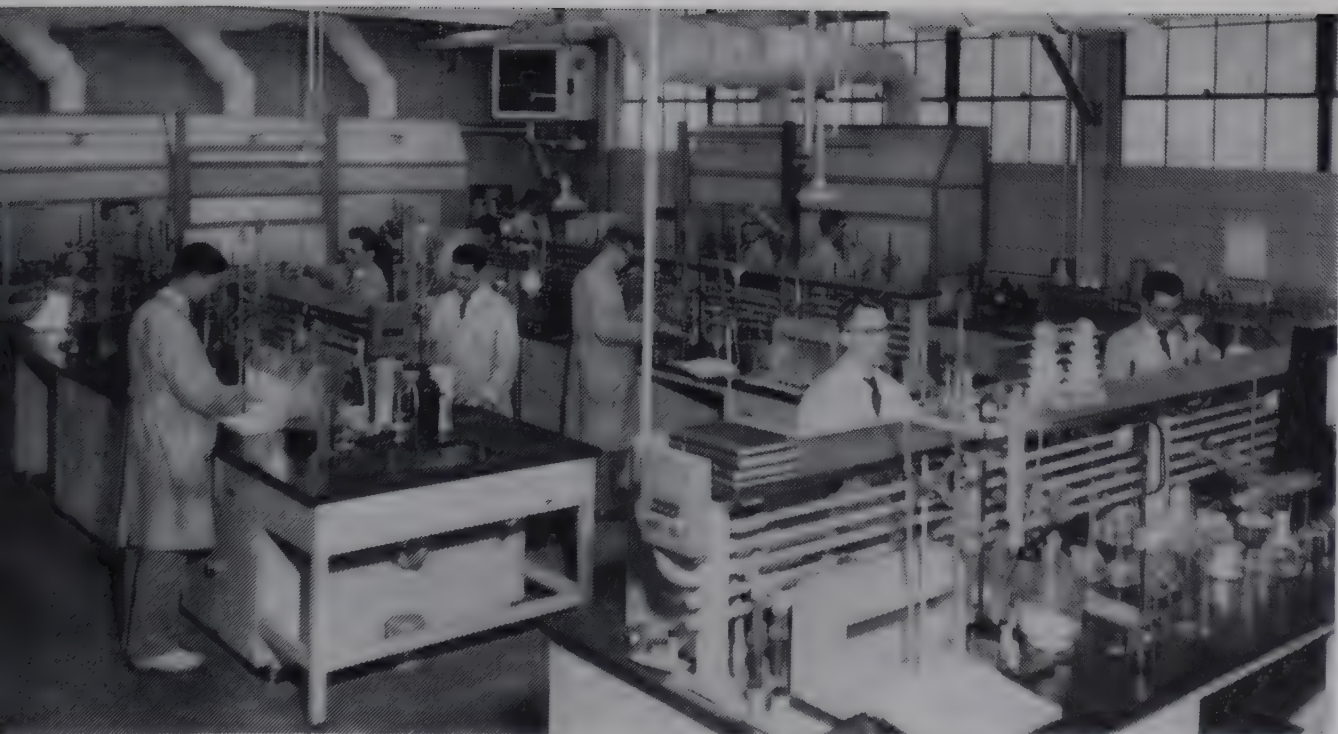
Solvent	G./100 G. Solvent
Water	19.3
Methanol	0.7
Ammonia (−30° C.)	20.0
Ether	Insoluble
Hydrocarbons	Insoluble
Dimethylformamide	1.1



Centrifuged down to 6% moisture, the next step is to dry potassium borohydride under vacuum. At times it must be held for awhile so it is stored in 55-gallon polyethylene-lined drums



Methanol is recovered in this still



Metal Hydrides relies heavily on analytical inspection to measure product quality. As the process is semicontinuous, a quality control program with electronic data processing equipment cannot be used advantageously

Maintenance Requirements Not Severe

Metal Hydrides has a regular maintenance schedule to keep its equipment in operating condition. This calls for biweekly lubrication of vital parts such as stuffing boxes and agitator packing glands. One man has this responsibility. Also, he checks fan belts, gear reducers, equipment oil levels, and makes visual observations to see that equipment functions properly.

Once a week the centrifuge is stripped down and cleaned. It accumulates solids in use.

During the company's annual vacation shut down, Metal Hydrides has a yearly equipment clean-up. All process units are shut down and cleaned. New packings are put in stuffing boxes. Tanks are pressure tested.

All units are visually inspected to check for failures. Tank covers are removed so workers can look inside. Included on the program are checks of other vital process units such as valves, seals, and gages.

Safety Is Important

Metal Hydrides has four hazardous areas in the manufacture of potassium borohydride:

- ▶ Hydrogen accumulation through leaks of any sort
- ▶ Methanol vapors after the sodium borohydride-oil mixture is hydrolyzed
- ▶ Handling liquid sodium
- ▶ Handling caustic soda

Metal Hydrides has taken the maximum precautions to prevent injury to its employees or damage to the plant. All tanks and reactors have safety relief valves set at 20% above operating pressures. Also, all tanks have vent lines with rupture disks set 10 to 15 pounds above the relief valve to handle any sudden surge in pressure. Most tanks have had vents tied to the central venting system which vents outdoors.

To guard against hydrogen leaks, continuous hydrogen monitor is located in the process area. It is set to shut down hydrogen flow and the plant's electrical system, if hydrogen concentration should reach 2%. The area is safe with concentrations up to 4%.

Also, Metal Hydrides has a portable hydrogen detector to find leaks in local areas. As a further precaution, air in the process area is replaced every 5 minutes.

All tanks are tied to a nitrogen smothering system. Electrical equipment is explosion proofed. Instrument controls are air operated.

For employee protection, Metal Hydrides provides Dynel (antistatic) work clothes. These garments are fireproofed. All employees wear safety goggles and plastic helmets. Plastic gloves are provided when workers handle caustic soda.

Many process areas have a master electric switch which shuts down hydrogen flow and all equipment except ventilation blowers and lights. And no smoking is allowed on plant grounds, except in a few selected and marked areas.

Analytical Program

Since Metal Hydrides' potassium borohydride process is semicontinuous, subject to sales demand, a quality control program, with electronic data processing equipment, cannot be used advantageously. But product quality is rigidly controlled. With a semicontinuous process it is a simple matter to find errors. Metal Hydrides leans heavily on analytical inspection to measure product quality. Here are the crucial process points which must be watched and the tests performed.

Oil for Dispersion. Spot checked from time to time. When it arrives at the plant oil is tested for refractive index, water content (Karl Fischer titration) and clarity (usually a visual inspection). Before re-use in the process it is again tested for water content and inspected for solids. If solids are present, oil is filtered before re-use.

Sodium Hydride. Tested each 8-hour working shift for concentration and assay.

Methyl Borate. Chief concern is water or methanol as impurities. Water is tested via Karl Fischer titration. Methanol is checked by sodium hydride reaction (normal level, 1.5% or lower).

Sodium Borohydride Reactor. Each 8-hour shift. Test for sodium borohydride content (usually less than 10%). Two tests can be used:

1. Water reaction—to tell how much sodium hydride is not converted
2. React with 50% hydrochloric acid

Water Solution before Crystallizer. Once a day when on stream. This is also a test for sodium borohydride content—here usually less than 20%.

Final Product. Test for purity after each batch is dried. Minimum specifications call for 97% purity, but product runs about 98.5%. Tests—potassium iodate reaction and hydrogen evolution. If product is "off-specs," the last process step is repeated.

Recovery Methanol. Each batch is tested for water content re-use in the process. Again the Karl Fischer test is used or, if water content is high, a methoxy group determination.

All process tanks have tap lines. All vessels have agitators, hence samples are always well mixed. Solid samples are obtained with a conventional grain sampler.

process. Sometimes the oil must be filtered before re-use.

Meanwhile the product liquor—which is now an aqueous-methanol solution of sodium borohydride and caustic soda—is pumped to a crystallizer, a 100-gallon stainless steel tank with an agitator.

Stoichiometric amounts of 50% potassium hydroxide are added to the solution in the crystallizer to convert potassium borohydride. About 85 to 90% of the potassium borohydride precipitates almost immediately. The mass is then dropped into a centrifuge located directly below the crystallizer.

The centrifuge operates at speeds between 750 and 1500 r.p.m. A 90- to 100-gallon batch can be centrifuged to about 6% moisture in 1 hour. Methanol-caustic soda solution is swirled out and pumped to a 200-gallon storage tank to await methanol recovery. The caustic solution is not worth recovering until the process is run on a much larger scale.

Meanwhile the moist potassium borohydride is dropped into a scow and transferred to a vacuum oven. This unit is steam heated to 130° C. The product dries in about 8 hours. Potassium borohydride is then better than 98% pure. If not up to purity standards, the crystallizing step is repeated until high purity is obtained.

The product is then transferred to the packaging department. Since it is non-hygroscopic, it can be handled and packaged in air. Metal Hydrides ships the product in quantities which range from 50 grams to 100 pounds. These amounts may be packaged in bottles, pails, or 55-gallon drums. Pails and drums are lined with polyethylene bags.

Acknowledgment

The authors are indebted to Lewis W. Davis for his permission to publish this article and also to Brad Arthur for his cooperation in its preparation.

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Dualayer Gasoline Process to Remove Mercaptans

BRUCE F. GREEK

Associate Editor in collaboration with

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Magnolia Petroleum Co., Beaumont, Tex.

AS THE RACE for ever higher octane motor gasoline becomes more competitive, each factor contributing to octane rating gets a closer scrutiny. Because sulfur compounds have a very important effect on the responses to tetraethyllead, they received much attention over the past 25 years.

In the early 1940's, Ryan (6) conducted quantitative studies on how sulfur compounds influenced octane number in tetraethyllead susceptibility. Others (3-5) have also demonstrated the effect of sulfur in gasoline. For example, as little as 0.01% sulfur in its active forms added to an aviation gasoline containing tetraethyllead may lower the gasoline octane number by as much as 9 points.

Sulfur in gasolines can be removed in many ways. The method used depends on the nature of the sulfur compounds and the relative costs involved.

A class of sulfur compounds that has a very significant effect on gasoline octane response to tetraethyllead together with their disagreeable odor is the mercaptans. In addition to mercaptans present in crude petroleum, appreciable quantities of them form in thermal and catalytic cracking. In the catalytically cracked products the relative percentage of mercaptans present is high compared to other sulfur compounds. Their removal considerably improves the tetraethyllead response, particularly of the gasolines of high octane numbers.

Two general methods exist for eliminating mercaptans in petroleum products:

1. Convert to disulfides
2. Remove with suitable chemical reagents.

The first method, usually referred to as "sweetening," gives disulfides which remain dissolved in the gasoline. These disulfides are odorless, but their effect on the tetraethyllead response of the gasoline is at least as damaging as that of the mercaptans. In addition the disulfides are very harmful to the gasoline stability.

The second method—removal of mer-

captans—is one of the most important in modern petroleum refining technology. Earlier processes developed for that purpose are either expensive or effect only a partial removal of the mercaptans. For this reason systematic research on mercaptan removal from petroleum distillates began in 1949 at the Process Engineering Laboratories of the Magnolia Petroleum Co., Beaumont, Tex. When the refinery faced the problem of increasing the octane rating of gasoline, the new process, known as the Dualayer gasoline process, was approved for installation. Simplicity of this process permitted construction of the commercial unit on the basis of laboratory data thus eliminating the pilot plant stage of development (7).

Operation of the first commercial unit which had a designed capacity of 30,000 barrels of gasoline per day proved very successful. Since going on stream in February 1956, the Dualayer gasoline treating unit capacity of the refinery has been increased to 38,000 barrels per day.

Chemical and Physical Considerations of Mercaptan Removal

Mercaptans present in light petroleum distillates such as gasoline are very weak acids and their acidity falls off rapidly with increased molecular weight. Acid materials in petroleum can be extracted partially with solutions of alkalis in water. With acid constituents such as mercaptans, the alkaline solvents form unstable chemical compounds which are separated from the alkaline solutions by steam distillation or other methods. Unfortunately, as the acidity of these compounds becomes weaker, they become more difficult to extract from petroleum but are easier to separate from the alkaline solutions.

The solubility of the mercaptans can be increased by adding cresylic or similar organic acids to the alkaline solution. (Cresylic acid refers to a mixture of phenol and *o*-, *m*-, and *p*-cresols.) In the Dualayer process the composition

of the alkaline solvent is adjusted to make it highly effective for the extraction of mercaptans.

In the Dualayer process, gasoline and a caustic-organic acid solution are contacted in the liquid phase and then separated. Mercaptans from the gasoline now in the spent treating solution are removed without further contacting with caustic. The caustic-organic acid solution is not soluble in gasoline and distillation of the refined gasoline to remove residual treating solution is not necessary.

The Dualayer gasoline treating process differs from conventional extraction processes in that it uses two immiscible but closely related solvents—hence its name. One of these solvents (a water solution of potassium hydroxide and potassium cresylate) contacts the gasoline to remove the mercaptans. The second solvent (potassium hydroxide in water) maintains the first solvent at a constant composition to maintain maximum extractive ability.

These two solvents are prepared by first producing an aqueous potassium hydroxide solution of high concentration and saturating this solution with cresylic acid until two layers are formed. The upper layer contains potassium cresylate, water, and potassium hydroxide, and is used to extract the mercaptans. The lower layer of potassium hydroxide and water acts merely as an auxiliary to the treating solutions and has no direct contact with the gasoline. Water and potassium hydroxide migrate between the two layers to reach equilibrium.

The phase diagram for potassium hydroxide, potassium cresylate, and water, Figure 1, shows the composition of the potassium cresylate-potassium hydroxide layer at which the separation of the two layers takes place, and also which represents the most effective solvent composition for mercaptan extraction.

Figure 2 shows a typical family of curves for mercaptans left in gasoline after being contacted with treating solutions of various potassium hydroxide,



Gasoline and Dualayer treating solution (potassium cresylate, water, and potassium hydroxide) are contacted countercurrently in mixing valves and separated in tanks in the foreground. The separating surge tank and the stripping tower are in the left center

potassium cresylate, and water ratios.

Viscosity increases as potassium cresylate concentration is increased. Too high a viscosity prevents good separation of the treating solution from the gasoline. Separation is very good with viscosity below 12 centistokes at 100° F. However, satisfactory operation can be obtained with viscosities as high as 150 centistokes at 100° F. As the composition approaches the two-phase line, extractive efficiency is highest for a given viscosity. At point *A* in Figure 2 or a typical composition in the commercial unit, viscosity is about 10 centistokes at 100° F. Extractive power for the mercaptans and the viscosity of the solutions are the two most important factors in determining solvent compositions.

In most caustic gasoline treating systems, the water content of the treating solution is varied to adjust compositions of the treating solutions. If only the water content were controlled in the Dualayer process, the potassium hydroxide and cresylate ratio would vary over a wide range. However, the Dualayer process can control the water, potassium hydroxide, and potassium cresylate contents. Water in the treating solution is controlled by the tempera-

ture and pressure of the stripper. Potassium hydroxide and potassium cresylate compositions of the treating solution depend on the equilibrium of the potassium hydroxide-water layer in the vessel where the stripped treating solution is recontacted with the potassium hydroxide solution. Thus, the Dualayer solution has one degree of freedom only—the total water content of the two layers at equilibrium.

Potassium hydroxide is used in the Dualayer process instead of sodium hydroxide for two reasons. Highly concentrated potassium hydroxide-potassium cresylate solutions have lower viscosities than sodium hydroxide solutions of similar concentrations. Losses due to entrainment are thus less for potassium hydroxide solutions. The potassium cresylate solutions also have higher extractive power than comparable solutions based on sodium hydroxide for any given viscosity level.

Because the treating solution in the Dualayer process has an extremely high capacity to remove mercaptans, the amount of treating solution required is low—less than 5% by volume for most applications. Because the volume of treating solution used is low, consumption of regeneration steam also is low—nor-

mally below 8 pounds per barrel of gasoline treated.

Magnolia's Commercial Unit

Figure 3 gives a modified flow sheet of the commercial Dualayer unit at Magnolia Petroleum Co.'s Beaumont, Tex., refinery. The flowsheet shows a two-stage prewash and a two-stage treating system. However, the commercial unit has three parallel Dualayer treating systems tied to a common regeneration system and each treating system may have one or two prewash stages depending on the amount of hydrogen sulfide and organic acids present in feed gasolines. Planned modifications include two prewash stages for each treating system. This will always leave a prewash stage on stream while the other is charged with caustic or shut down for repairs, thus preventing any possible contamination of the potassium cresylate treating solution.

Gasoline Treating. Gasolines to be treated in the Dualayer unit come directly from other preliminary refining units. They are mixed with sodium hydroxide in an orifice mixer (1E) and go to the first separating tank in a prewash stage. Concentration of sodium hydroxide used in the prewash stages varies with the quantities of hydrogen sulfide

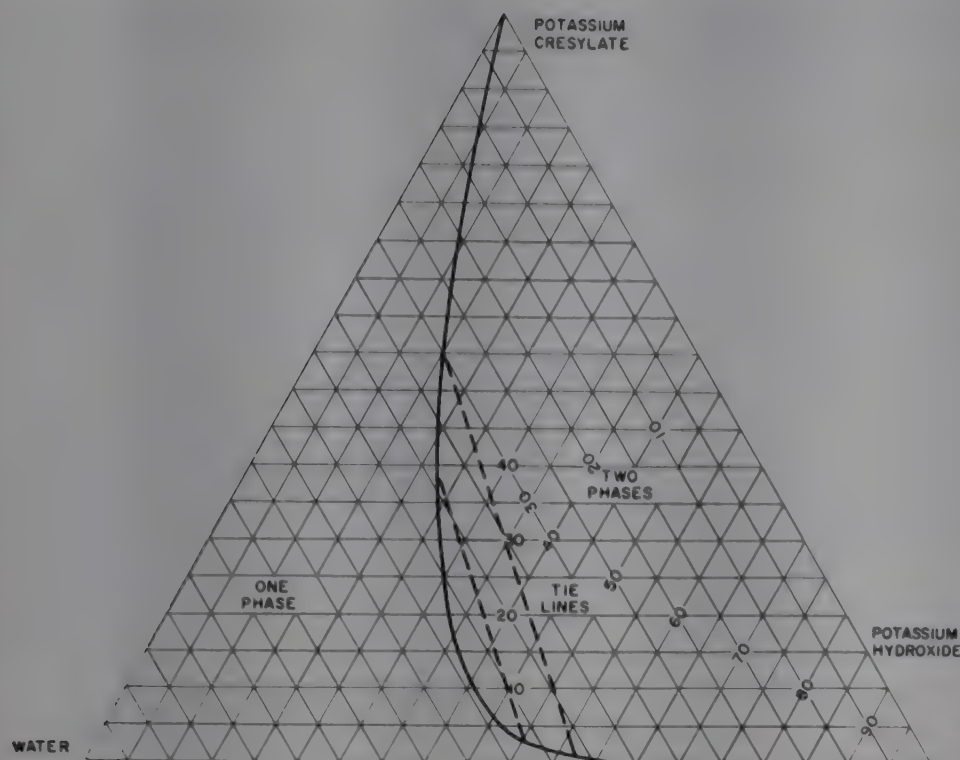


Figure 1. A phase diagram of water-potassium hydroxide-potassium cresylate

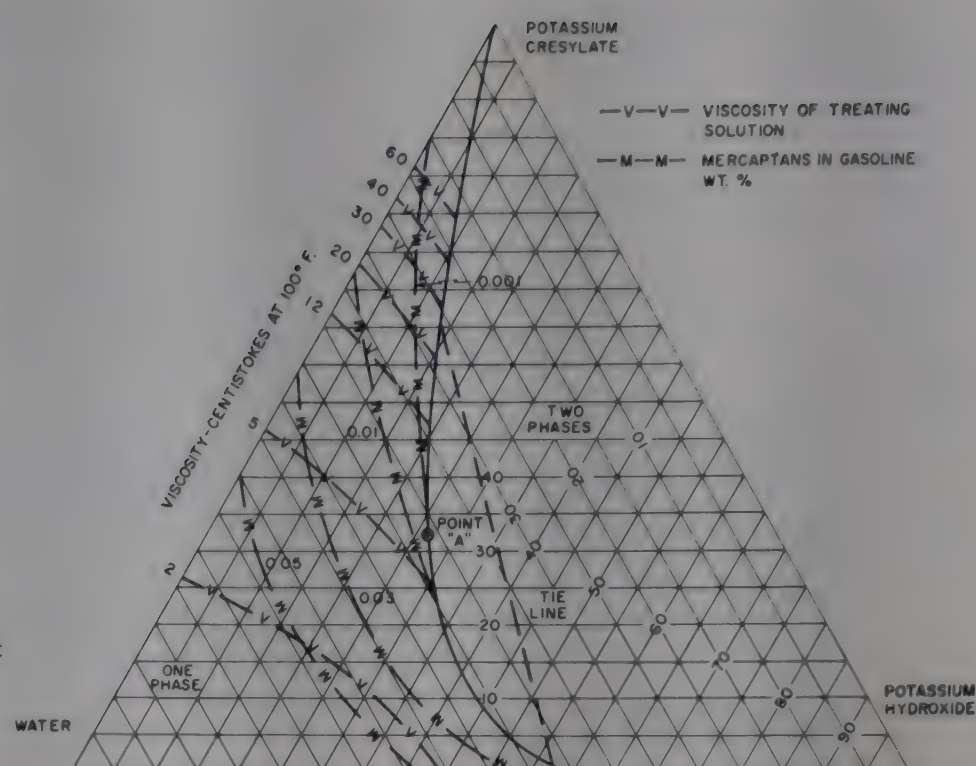


Figure 2. Viscosity curves of Dualayer treating solution and mercaptan contents of gasoline at equilibrium with treating solution

and organic acids present in the gasolines. However, sodium hydroxide concentration is kept low to minimize the carry-over into the treating solution.

In the separating tank, unreacted sodium hydroxide and sodium sulfide are taken from the bottom and recycled. As sodium sulfide concentration rises, the prewash solution is drawn off and sent to waste, while another stage carries the cleaning load.

From the prewash stages, the gasoline goes to a coalescer to remove traces of water, sodium hydroxide, and sodium sulfide. The coalescer is filled with fiber glass to improve separation.

From the coalescer, the gasoline goes to a final settler before contacting the Dualayer treating solution. Again orifice mixers are used to contact the gasoline with the potassium cresylate treating solution. Two mixers are used in parallel for each contacting stage. Countercurrent contacting uses the partially spent potassium cresylate to first contact the gasoline. Two contacting stages are used. Between each mixing stage, a separating tank removes most of the potassium cresylate treating solution from the gasoline. As the treating solution amounts to no more than 3% of the volume of gasoline, good separation is important.

After the treated gasoline leaves the last separation tank, it goes to a final settling tank. The treating solution has such a low solubility in gasoline that settled, treated gasoline has practically no carry-over treating solution and no components of the treating solution left in it. From the final settling tank, the gasoline goes to product blending.

Treating Solution Regeneration. Spent potassium cresylate solution from the separation tank for the first contacting stage is diluted with hot water from

the stripping tower. Diluting the treating solution with hot water helps to separate traces of emulsified gasoline in the solution and provides stripping steam.

In the separator surge tank, carry-over gasoline goes to the top and returns to the first set of orifice mixers in the treating system. Because of the high dilution permitted by exceptionally low circulation of treating solution, virtually all gasoline is removed from the solution prior to regeneration.

Part of the spent potassium cresylate treating solution, as it comes from the separator surge tank, is taken off and pumped through a leaf filter (2E). The filter uses a two-layer precoat of wood pulp. The first layer is 40-mesh pulp and the second 100-mesh. Iron sulfides and other unidentified solids are removed by the filter. These finely divided materials contribute to emulsions in the treating system and must be efficiently removed. The filter is routinely dumped once a week.

The diluted spent treating solution, after preheating, is charged to the stripping tower on the ninth tray from the bottom. A small quantity of light lubricating oil is added with the feed to prevent foaming.

The stripping tower contains 11 Uniflux trays (3E). It is six feet in diameter. A closed reboiler is used with steam at 150 pounds per square inch gage for supplying heat. Although actual operating conditions vary, overhead steam and mercaptans leave at about 232° F. and 8 pounds per square inch gage.

From the top of the tower, steam and mercaptans are condensed and partially cooled in a heat exchanger that is air-cooled. More cooling is done with a water-cooled exchanger.

Condensate and vapors go to an over-

head accumulator. Three layers exist in the accumulator. The top layer contains noncondensable gases under low pressure which are piped to a gas recovery system in the refinery. The middle layer consists largely of liquid mercaptans predominantly in the C₃ and C₄ range. These are either sold or burned in the power house. The lower level is water returned to the tower on the top tray as reflux.

From the tower's tenth tray, hot dilution water is taken off. Mercaptan content of dilution water is so low that its effect on gasoline separation in the separator surge or on stripping is negligible.

The stripped and concentrated potassium cresylate solution comes from the tower bottom and passes through a water-cooled exchanger. From the exchanger it goes to a circulating system for the potassium hydroxide-water layer in the potassium hydroxide-potassium cresylate contactor. A mixing valve is used to mix the potassium cresylate treating solution with the potassium hydroxide-water layer. Here the treating solution returns to maximum strength to extract mercaptans. In the contactor, the potassium cresylate solution separates.

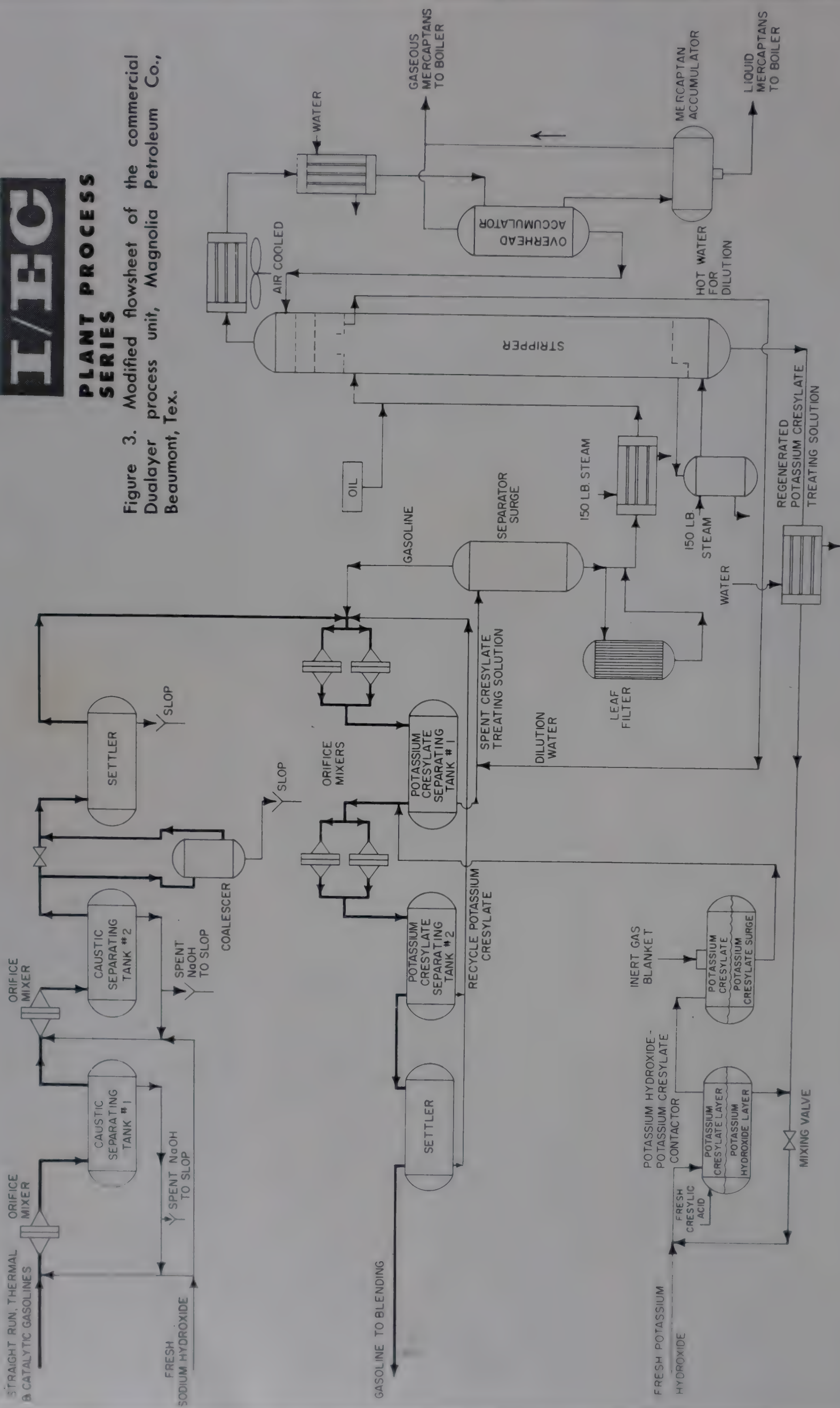
From the contactor, regenerated potassium cresylate solution is pumped to a storage tank and held until needed under a blanket of inert gas to minimize oxidation.

For normal operation, between 150 and 200 barrels of treating solution are kept ready for use. This quantity will permit the stripping tower and other parts of the regeneration system to be shut down for at least 8 hours without mercaptan content of treated gasoline showing an appreciable increase.

A summary of operating conditions is given in Table I.

PLANT PROCESS SERIES

Figure 3. Modified flowsheet of the commercial Dualayer process unit, Magnolia Petroleum Co., Beaumont, Tex.

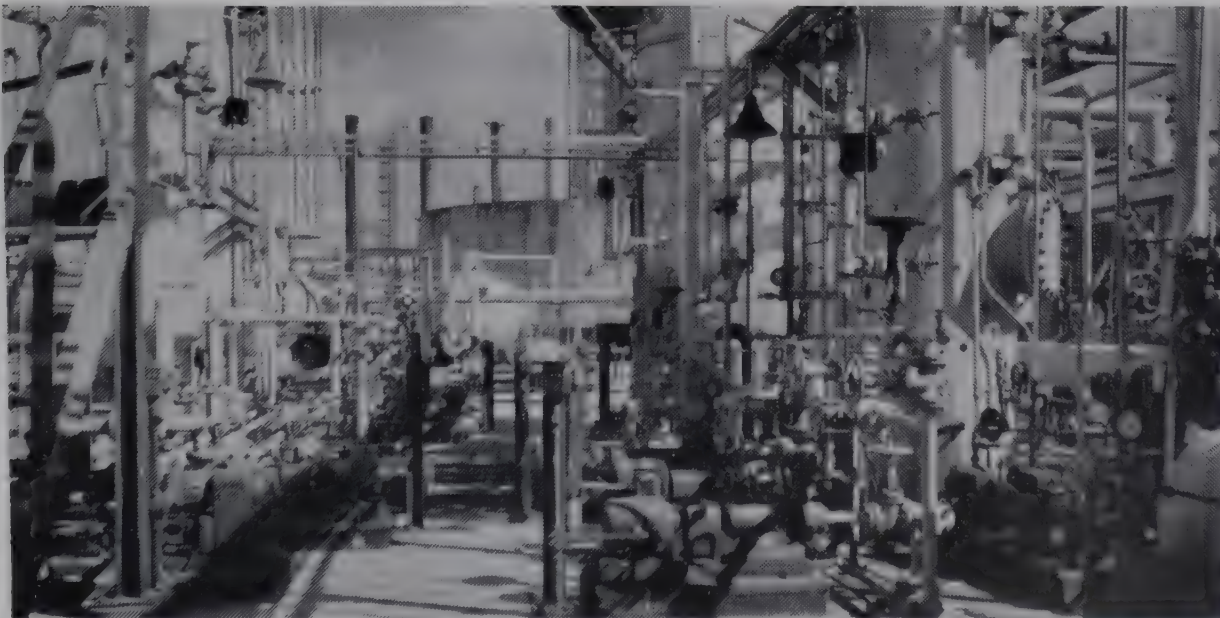




In the Dualayer gasoline treating process, gasolines are first treated and separated from caustic in horizontal drums. The caustic treated gasoline goes to a coalescer (vertical tank behind control room) before being contacted with the Dualayer potassium cresylate treating solution. The treating solution after leaving the final separator, is diluted with hot water and is passed through a leaf filter (left of control house). From the filter it goes to the stripping tower which appears behind the control house.



After the gasoline leaves the caustic-treating section, it is contacted in orifice mixers with potassium cresylate treating solution and is separated from the treating solution in tanks at left. Each Dualayer gasoline treating section uses two separating tanks, as the gasoline is treated countercurrently. Immediately behind the control house at right is the mercaptan stripper



Pumps and manifolding in foreground direct the flow of treating solutions and dilution water in the Dualayer gasoline treating unit. The separator surge tank (at left behind condensate tank) removes last traces of gasoline from the diluted treating solution before it goes to the stripping tower in center

Table I. Operating Conditions for Dualayer Gasoline Treating

Treating Section	
Oil rate, barrels/day	38,000
Dualayer solution rate, barrels/day	1,000
Extraction stages	2
Extractor pressure drop, lb./sq. inch gage/stage	10
Extractor temperature, ° F.	120
Regenerating Section	
Stripper charge, barrels/day	
Spent Dualayer solution	1,000
Dilution water	700
Total	1,700
Temperature, ° F.	
Reboiler out	324
Tower bottom	320
Preheater in	170
Preheater out	274
Feed tray	266
Dilution take-off tray	234
Reflux	104
Tower top	230
Overhead condenser out	190
Gravity, ° Bé.	
Dualayer solution	39.5
Potassium hydroxide solution	49.5

Corrosion. Except for hot potassium hydroxide service, corrosion in the Dualayer process compares similarly with that generally found in a modern refinery. Mild steel is used in all tanks, lines, pumps, and other processing equipment except for parts of the regeneration system.

Monel is used for the stripper preheater, reboiler, and bottoms pump. All trays in the tower are Monel. For a distance of 10½ feet from the bottom, the tower is Monel-lined and stress-relieved.

Instrumentation. The Dualayer unit is instrumented to require a minimum of operator attention. Separator tank interface levels are controlled to obtain best possible separation between the two layers. The separator surge drum has the spent potassium cresylate layer controlled near its top. This allows virtually all gasoline to break from the diluted treating solution yet allows none of the potassium cresylate to return with the gasoline.

The stripper tower has the bottoms and dilution water take-off tray (tray 10) level controlled. Tower feed, reboiler, bottoms, reflux, and overhead temperatures are indicated. Some of these temperatures are controlled by a cooling water flow, steam input, and reflux volume adjustments.

Operating Results and Economics. Since the unit was placed on stream, the fraction of gasoline treated by the Dualayer process has gradually increased until all of the high mercaptan content motor gasoline produced at the

Beaumont refinery is treated. Other treating facilities to sweeten gasolines have been converted to other uses. Over 98% of the mercaptans present are removed from sour thermal, straight run, and catalytic gasolines. In some instances, the antiknock rating of final gasoline has been raised by as much as four octane numbers.

In addition to mercaptan removal, potassium cresylate also takes virtually all alkali phenols from the gasoline. This improves gasoline cloudiness and response to synthetic inhibitors.

Typical results obtained on treating various gasolines by the Dualayer unit are given in Table II.

Direct cash operating costs for the process based on a year's experience are given in Table III. Operating labor cost is particularly low. Approximately two thirds of an operator's time per shift is required to operate the unit. However, several operators are in the Dualayer unit area and they may co-operate to run the unit under special conditions or during any period of unbalance due to shut down of equipment. Usually the only routine tests made by an operator are a check of the prewash effluent to ensure removal of all hydrogen sulfide, and a mercaptan content on product gasoline.

Table IV shows the effect on refinery economics of replacing a mercaptan to disulfide conversion-type process with the Dualayer unit. Values of octane number increase and tetraethyl lead savings are very conservative. If the effect of raising the ratio of premium to housebrand gasoline were included, a more attractive revenue increase results.

Process Future

The Dualayer process was developed for a specific application—that of mercaptan removal from a relatively limited molecular weight range of hydrocarbons found in gasoline.

At present, variations of the process in commercial use include treating o heavier petroleum distillates to remove phenols and other acidic materials that contribute to instability as well as mercaptans (2). Here the salts formed by reaction of acidic materials with potassium or sodium hydroxide such as cresylates are discarded along with mercaptans after separation from caustic-treating solutions. In this application, the second layer that results from adding phenolic compounds to concentrated potassium hydroxide is formed during the contacting of distillates with potassium hydroxide.

Potential uses for this low cost method for separation of mercaptans and other acidic organic compounds in small quantities from large amounts of hydrocarbons are widely varied. Lique-



Mercaptans are stripped from the potassium cresylate Dualayer treating solution in an 11-tray tower. Near the top of tower hot water is taken off to dilute the spent treating solution which gives almost complete separation of gasoline from the treating solution. The dilution water also provides stripping steam

Table II. Magnolia Dualayer Unit Charge and Product Properties

	Type of Gasoline					
	Straight Run		St. Run-Thermal		Catalytic	
	Charge	Product	Charge	Product	Charge	Product
Gravity, ° API		73.6		70.5		58.8
RVP, lb./sq. inch abs.		9.6		10.0		8.2
Distillation, ° F.						
IBP		106		104		111
10%		125		126		133
50		158		172		216
90		226		246		352
EP		346		340		408
Mercaptan sulfur, wt. %	0.052	0.0020	0.036	0.0017	0.011	0.002
Total sulfur, wt. %	0.06	0.01	0.07	0.04
Octane, research 3 ml. TEL	85.5	87.3	87.3	88.8	96.6	97.0

Table III. Operating Costs on 38,000-Barrel-Per-Day Dualayer Unit

	Cost, Cents Barrel
Operating labor	0.37
Maintenance	0.14
Chemicals	
Sodium hydroxide	0.43
Potassium hydroxide	0.36
Cresylic acid	0.16
Other	0.12
Utilities	
Steam	0.29
Power	0.02
Water	0.07
Product loss (computed as gasoline)	0.16
Total cash costs	2.12

Table IV. Typical Savings for Dualayer Gasoline Process over Sulfur Conversion Process

	Method of Treatment	
	Conversion	Dualayer
Sulfur, wt. %		
Mercaptan or disulfide	0.044	0.002
Total	0.08	0.04
Octane, research, 3 ml. TEL	92.0	93.5
At 92 research octane		
Required TEL, ml./gal.	3.00	1.87
In TEL		
Cost, ¢/barrel	...	10.5
\$/1000 barrels	...	105

fied petroleum gases recovered from wet natural gas may be improved by immediate removal of mercaptans. With only minor separation difficulties, the process can be adapted to mercaptan removal from jet fuels to improve their stability and odor. The Dualayer process could also be adapted to process products from coal tar distillation for removal of sulfur compounds as well as to separate phenolic compounds.

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Processing Equipment

- (1E) Duriron Co., Dayton 1, Ohio, orifice mixer.
- (2E) Niagara Filters, Div. of American Machine and Metals, Inc., East Moline, Ill., leaf filter.
- (3E) Socony Mobil Oil Co., Inc., New York, N. Y., Uniflux trays.

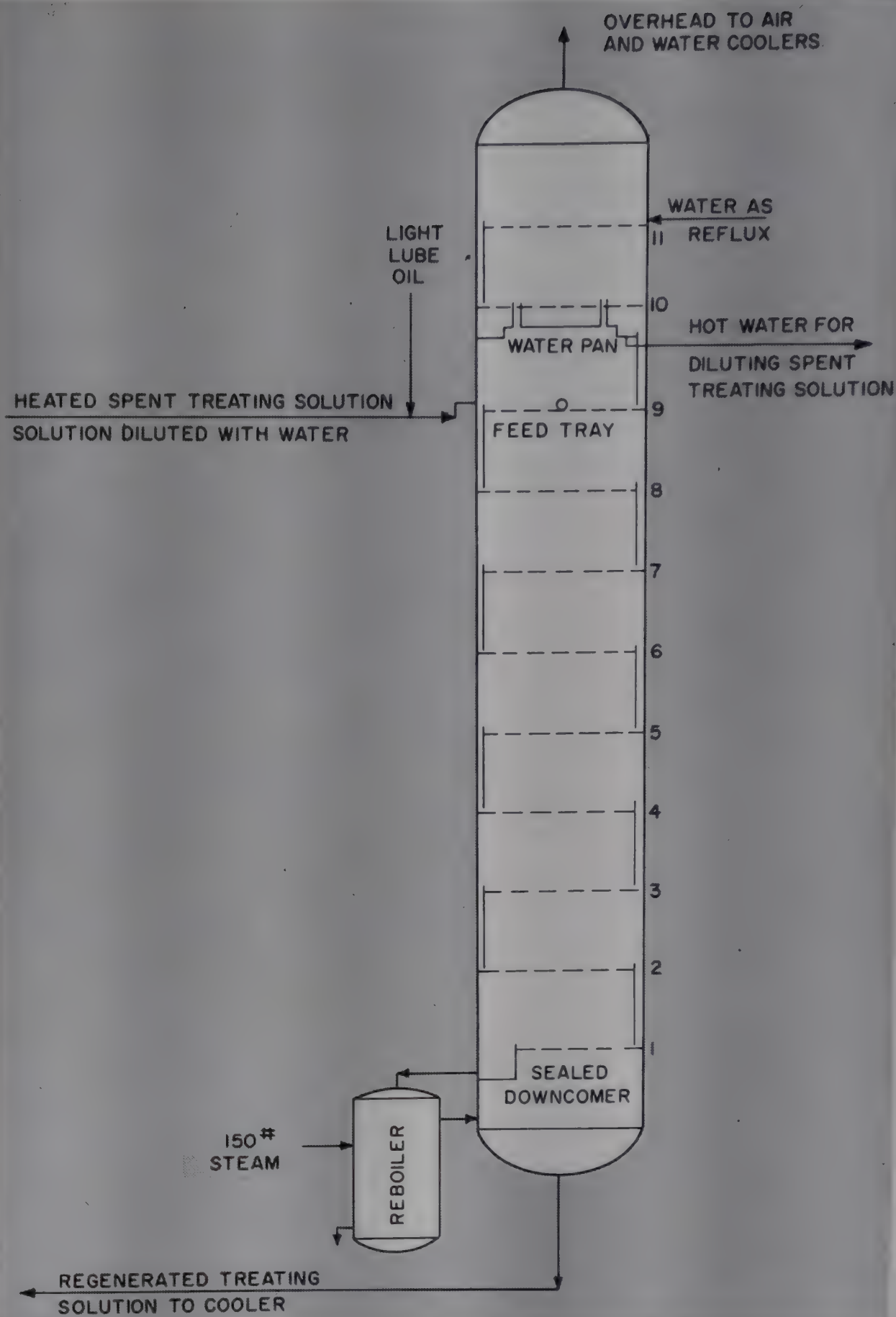


Figure 4. The stripping tower is used to remove mercaptans from the Dualayer treating solution. This is done by steam stripping in a tower, 6 feet in diameter, containing 11 Uniflux trays

All stripping steam is supplied by the water used to dilute spent treating solution. A preheater raises feed temperature to above 260° F. which causes some flashing of the feed after it enters the tower on tray 9 (numbered from the bottom). Trays 10 and 11 effectively are heat exchangers where water reflux takes heat from steam and mercaptans in the overhead vapor

A water pan or reservoir below tray 10 collects hot water to be pumped into the line carrying spent treating solution from the second gasoline-treating solution contactor to the separator surge tank. By having the hottest water possible from the tower for dilution, heat needed for stripping remains at a minimum

Take-off for reboiler feed comes from a larger sealed downcomer under tray 1. Reheated treating solution from the reboiler returns to the tower near its bottom where the last of the mercaptans and some additional water vaporize. Regenerated treating solution is taken off at the tower's bottom

Light lube oil is added to the heated feed to prevent foaming. When the Dualayer unit operates at capacity, about 5 gallons of lube oil per day are used

◀ The Dualayer gasoline treating unit is highly instrumented so that only two thirds of an operator's time per shift is needed to operate the unit

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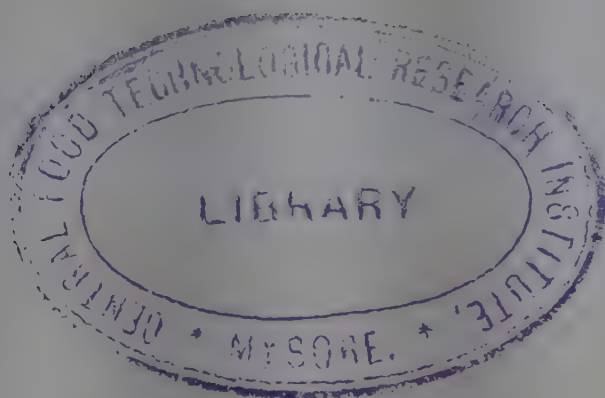
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